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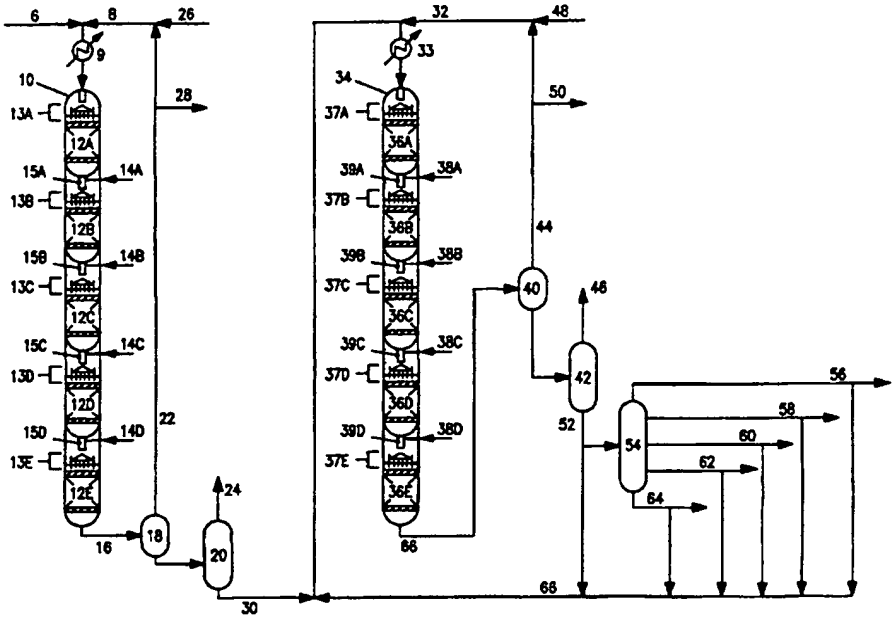

(57) Abstract

A process for upgrading oil feedstock which contain more than 50 % virgin oils, wherein the feedstock is hydrocracked to adjust the hydrogen content, flashed and/or hydrocracked to adjust the hydrogen content. Employing a vertical reactor shell (10) encloses and supports a stacked series of fixed porous solid beds of solid hydrotreating catalyst, as depicted by (12a) through (12e). A chargestock (6) is combined with a hydrogen rich gas (8) and introduced to the reactor (10) after undergoing appropriate heating means (9).

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INTEGRATED LUBRICANT UPGRADING PROCESS

This invention relates to the hydrocracking and subsequent catalytic dewaxing of petroleum chargestocks. In particular, it relates to an integrated fuels hydroprocessing scheme which comprises hydrocracking, distillation, catalytic dewaxing and hydrofinishing steps. A dewaxed product of improved viscosity index stability, color and lower volatility is produced. The hydrocracker increases the hydrogen content, reduces the viscosity and lowers the boiling range of the hydrocracker charge stock. The catalytic dewaxer selectively cracks and/or hydroisomerizes the waxy hydrocrackate. The hydrofinisher hydrogenates aromatics and olefins. It reduces the ultraviolet light absorptivity of the dewaxed oil. Distillation is used to adjust volatility. The resulting lube base oil product is water-white, has low aromatics content, low pour point, improved cold flow properties, high viscosity index, low volatility and excellent oxidation stability.

Mineral oil lubricants are derived from various crude oil stocks by a variety of refining processes directed towards obtaining a lubricant base stock of suitable boiling point, viscosity, pour point, viscosity index (VI), stability, volatility and other characteristics. Generally, the base stock will be produced from the crude oil by distillation of the crude in atmospheric and vacuum distillation towers, followed by the removal of undesirable aromatic components by means of solvent refining and finally, by dewaxing and various finishing steps. Because multi-ring aromatic components lead to poor thermal and light stability, poor color and extremely poor viscosity indices, the use of crudes of low hydrogen content or asphaltic type crudes is not preferred as the yield of acceptable lube stocks will be extremely low after the large quantities of aromatic components contained in the lubestocks from such crudes have been separated out. Paraffinic and naphthenic crude stocks are therefore

preferred but aromatic treatment procedures are necessary with feedstocks which contain polynuclear aromatics in order to remove undesirable aromatic components.

In the case of the lubricant distillate fractions, generally referred to as the neutrals, e.g. heavy neutral, light neutral, etc., the aromatics may be extracted by solvent extraction using a solvent such as furfural, N-methyl-2-pyrrolidone, phenol or another chemical which is selective for the extraction of the aromatic components. If the lube stock is a residual lube stock, the asphaltenes will first be removed in a propane deasphalting step followed by solvent extraction of residual aromatics to produce a lube generally referred to as bright stock. In either case, however, a dewaxing step is normally necessary in order for the lubricant to have a satisfactorily low pour point and cloud point, so that it will not solidify or precipitate the less soluble paraffinic components under the influence of low temperatures.

Lubricant base stocks of high viscosity index(VI) may be manufactured by the processing of fuels hydrocracker bottoms. This route provides the potential for the manufacture of base stocks with VI of 115 or greater. The fuels hydrocracking scheme of the instant invention not only improves VI, but provides a means to meet new international guidelines regarding lower volatility base stocks e.g., ILSAC GF-2. The newly proposed volatility requirements require the removal of lighter, lower boiling lube fractions than currently practiced in vacuum distillation procedures for the preparation of lubricant basestocks and this increases their viscosity. Consequently, higher boiling, higher viscosity material must also be removed in the distillation procedures in order to maintain viscosity. This generally leads to lower yields and narrower cuts of lube basestocks and this increases their viscosity. Distillation of the hydrocracker bottoms, as disclosed in the instant invention, with return of non-lube range material to the

hydrocracker as recycle (or passage to a second hydrocracker), can also improve the operability and efficiency of the hydrocracker by removing undesirable components such as polynuclear aromatics. The resulting lube range fractions may then be catalytically dewaxed, hydrotreated, then distilled to produce the final lubricant product.

A fuels hydrocracking process with partial liquid recycle is disclosed in U.S. Pat. No. 4,983,273 (Kennedy et al.). In this the feed (usually vacuum gas oil(VGO)) or light cycle oil(LCO) is processed in a hydrotreating reactor, then in a hydrocracking reactor prior to being passed to a fractionator. A portion of the fractionator bottoms is then recycled to the hydrocracker. There is no teaching, as in the instant invention, of submitting the fractionator bottoms to an additional vacuum distillation step prior to additional hydrotreating or hydrocracking however.

Yukong Limited has disclosed (International Application PCT/KR94/00046) a method for producing feedstocks of high quality lube base oil from unconverted oil (UCO) of a fuels hydrocracker operating in recycle mode. As in the instant invention, a vacuum distillation unit is employed following fractionation. Various cuts of UCO from the vacuum distillation unit (UCO) are then recycled to the hydrocracker reactor. In the instant invention, any of the fractions from the vacuum distillation unit may be recycled to the first hydrocracker, passed to a second hydrocracker, or even to an FCC unit. The cuts from the vacuum distillation unit need not be recycled to the hydrocracker. The application of Yukong does not disclose the necessity of operating the fuels hydrocracker to produce waxy fuels hydrocracker bottoms which have the appropriate hydrogen content to obtain subsequently dewaxed basestocks having a VI of at least 115. Yukong claims further dewaxing and stabilization steps in general, but does not describe or

claim the specific catalytic dewaxing and subsequent hydrotreating techniques of the instant invention.

Catalytic dewaxing processes are becoming favored for the production of lubricating oil stocks. They possess a number of advantages over the conventional solvent dewaxing procedures. The catalytic dewaxing processes operate by selectively cracking the normal and slightly branched waxy paraffins to produce lower molecular weight products which may then be removed by distillation from the higher boiling lube stock. Concurrently with selective catalytic cracking of waxy molecules, hydroisomerization with the same or different catalyst can convert a significant amount of linear molecules to branched hydrocarbon structures having improved cold-flow properties. A subsequent hydrofinishing or hydrotreating step is commonly used to stabilize the product by saturating lube boiling range olefins produced by the selective cracking which takes place during the dewaxing. Reference is made to U.S. Patent Nos. 3,894,938 (Gorring et al.), 4,181,598 (Gillespie et al.), 4,360,419 (Miller), 5,246,568 (Kyan et al) and 5,282,958 (Santilli et al) for descriptions of such processes. Hydrocarbon Processing (Sept. 1986) refers to Mobil Lube Dewaxing Process, which process is also described in Chen et al "Industrial Application of Shape- Selective Catalysis" Catal. Rev.-Sci. Eng. 28 (283), 185-264 (1986), to which reference is made for a further description of the process. See also, "Lube Dewaxing Technology and Economics", Hydrocarbon Asia 4 (8), 54-70 (1994).

In catalytic dewaxing processes of this kind, the catalyst becomes progressively deactivated as the dewaxing cycle progresses. To compensate for this, the temperature of the dewaxing reactor is progressively raised in order to meet the target pour point for the product. There is a limit, however, to which the temperature can be raised before the properties of the product, especially oxidation stability become unacceptable. For this reason, the catalytic dewaxing process is usually operated in cycles

with the temperature being raised in the course of the cycle from a low start-of-cycle (SOC) value, typically in the range of 232°C to 274°C (450°F to 525°F), to a final, end-of cycle (EOC) value, typically 354-385°C (670-725°F), after which the catalyst is reactivated or regenerated for a new cycle. Typically, dewaxing catalysts which employ ZSM-5 as the active ingredient may be reactivated by hot hydrogen. Other dewaxing catalysts may be decoked using air, or oxygen in combination with N_2 or flue gas. Catalysts which contain active ingredients, such as ZSM-23 or SAPO-11, that are less active than ZSM-5 containing catalysts may have start-of-cycle (SOC) and end-of-cycle (EOC) temperatures that are 25 to 50°C higher than those that contain ZSM-5.

The use of a metal hydrogenation component on the dewaxing catalyst has been described as a highly desirable expedient, both for obtaining extended dewaxing cycle durations and for improving the reactivation procedure even though the dewaxing reaction itself is not one which requires hydrogen for stoichiometric balance. U.S. Patent No. 4,683,052 discloses the use of noble metal components e.g. Pt or Pd as superior to base metals such as nickel for this purpose. A suitable catalyst for dewaxing and isomerizing or hydro-isomerizing feedstocks may contain 0.1-0.6, wt% Pt, for instance, as described in U.S. Pat. No. 5,282,958; 4,859,311; 4,689,138; 4,710,485; 4,859,312; 4,921,594; 4,943,424; 5,082,986; 5,135,638; 5,149,421; 5,246,566; 4,689,138. In the instant invention, 0.2 to 1 wt.% Pt is preferred, although Pd is also acceptable.

Chemical reactions between liquid and gaseous reactants present difficulties in obtaining intimate contact between phases. Such reactions are further complicated when the desired reaction is catalytic and requires contact of both fluid phases with a solid catalyst. In the operation of conventional concurrent multiphase reactors, the gas and liquid under certain

circumstances tend to travel different flow paths. The gas phase can flow in the direction of least pressure resistance; whereas the liquid phase flows by gravity in a trickle path over and around the catalyst particles. Under conditions of low liquid to gas ratios, parallel channel flow and gas frictional drag can make the liquid flow non-uniformly, thus leaving portions of the catalyst bed underutilized due to lack of adequate wetting. Under these circumstances, commercial reactor performance can be much poorer than expected from laboratory studies in which flow conditions in small pilot units can be more uniform.

In refining of lubricants derived from petroleum by fractionation of crude oil, a series of catalytic reactions may be employed for severely hydrotreating, converting and removing sulfur and nitrogen contaminants, hydrocracking and isomerizing components of the lubricant charge stock in one or more catalytic reactors. Polynuclear aromatic feedstocks may be selectively hydrocracked by known techniques to open polynuclear rings. This can be followed by hydrodewaxing and/or hydrogenation (mild hydrotreating) in contact with different catalysts under varying reaction conditions. An integrated three-step lube refining process disclosed by Garwood et al, in U.S. Patent No. 4,283,271 is adaptable according to the present invention.

In a typical multi-phase hydrodewaxing reactor, the average gas-liquid volume ratio in the catalyst zone is about 1:4 to 20:1 under process conditions. Preferably the liquid is supplied to the catalyst bed at a rate to occupy about 10 to 50% of the void volume. The volume of gas may decrease due to the depletion of reaction H_2 as the liquid feedstock and gas pass through the reactor. Production of vapors from formation of methane, ethane, propane and butane from the dewaxing reactions, adiabatic heating or expansion can also affect the volume.

Summary of the Invention

An improved, integrated process for hydrocracking and hydrodewaxing high-boiling paraffinic wax-containing liquid petroleum lubricant oil chargestocks has now been found. Vacuum gas oils, light cycle oils or even deasphalted oils may be hydrocracked in a fuels hydrocracker scheme which comprises a downstream vacuum distillation unit. Catalytic dewaxer feedstocks having hydrogen above about 13.5 wt.% are produced from the fuels hydrocracker and subsequently dewaxed, hydrofinished and distilled. At least 50 weight percent of the feedstock is converted to hydrocarbon products which boil below the initial boiling point of the feedstock. The improved process comprises the steps of:

(a) passing the chargestock, which comprises vacuum gas oil (VGO) or light cycle oil (LCO) or deasphalted oil, to a fuels hydrocracking system, where it is hydrotreated at high pressure, then hydrocracked at high pressure prior to fractionation and subsequent vacuum distillation of fractionator bottoms to produce the desired viscosity and volatility;

(b) hydrodewaxing the fractions from the vacuum distillation unit in a stage where dewaxing and hydroisomerization may both occur by uniformly distributing and contacting the liquid chargestock at elevated temperature up to 425°C (797°F) in the presence of cofed hydrogen at a pressure of at least 10,000 kPa (1450 psi) with an acidic, shape-selective, medium pore molecular sieve hydro-dewaxing catalyst to obtain a dewaxed lubricant oil;

(c) hydrofinishing the dewaxed lubricant oil in a hydrofinishing stage under aromatics saturation conditions in contact with cofed hydrogen and an effective aromatics saturation catalyst having strong metal hydrogenation function.

By employing a start of cycle (SOC) hydrofinishing temperature of 230° C (446°F) to 343°C (650°F) and pressure of at least 10,000 kPa (1450 psi) a dewaxed lubricant oil

product (which boils above about 370°C) is obtained. After subsequent distillation, the dewaxed oil product has less than 5 wt% aromatics and enhanced oxidative stability, UV light stability and thermal stability. The product possesses a NOACK number of 20 or lower and a VI of 115 or higher. Viscosities are in the range from 3 to 10 cSt at 100°C.

The preferred hydrodewaxing catalyst comprises a molecular sieve having pores comprised of 10 oxygen atoms alternating with predominantly silicon atoms, such as aluminosilicate zeolites having the structure of ZSM-5, ZSM-23, or ZSM-35 or ZSM-48. Other non-zeolitic molecular sieves, such as SAPO-11, having similar pore size are also suitable catalysts. With the exception of ZSM-5, it is desirable that the catalyst comprise from 0.1 to 1 wt. % noble metal. The preferred hydrofinishing catalyst to be employed subsequent to dewaxing comprises at least one Group VIIIA metal and one Group VIA metal (IUPAC) on a porous solid support or Pt or Pd on a porous solid support. A bimetallic catalyst containing nickel and tungsten metals on a porous alumina support is a good example. The support may be fluorided.

As previously indicated, preferred feeds to the fuels hydrocracker are virgin gas oils, such as light vacuum gas oil (LVGO), vacuum gas oil (VGO) and heavy vacuum gas oil (HVGO). VGO and HVGO normally contain significant levels of polycyclic aromatics. After hydrocracking, and vacuum distillation the waxy material to be catalytically dewaxed usually has a VI of at least 125, preferably 130 or greater, contains about 1 to 15 wt% aromatic hydrocarbons, has a 10 vol% boiling point above about 315°C (600°F), and contains no more than 30 ppm nitrogen. It has a hydrogen content above about 14.0 wt%. At 100°C, it has a viscosity of greater than 3 cS.

The hydrodewaxed effluent is hydrofinished and distilled, then is separated to recover a lubricant product which boils above 370°C (698°F) having kinematic viscosity

(KV) in the range from 10 to 160 cSt at 40°C or 3 to 10 cSt at 100°C. The product lube oil has a UV absorptivity at 325 nm of less than 0.001 L/g-cm (L represents liters) and an aromatics content of 5 wt% or lower.

Advantageously, the dewaxing stage and hydrofinishing stage are operated at substantially the same pressure, and the entire dewaxed oil stream from the dewaxing stage can be passed directly to the hydrofinishing stage in a cascade operation.

The Drawings

Figure 1 is a schematic diagram of a fuels hydrocracker suitable for use in the instant invention. A hydrotreater, hydrocracker, separator, vacuum distillation unit and hydrofinisher are illustrated. Unconverted material from the fractionation unit may be recycled to the hydrocracker or may be sent to the vacuum distillation unit to be appropriately cut for feed to the catalytic dewaxing reactor.

Figure 2 is a simplified diagram showing a series of vertical reactors with fixed catalyst beds, showing major flow streams;

Figure 3 demonstrates the relationship between boiling point and viscosity for pure components and vacuum gas oils from Arab light crude.

Figure 4 presents a comparison of the features of small pore, medium pore and large pore zeolites, or molecular sieves

Figures 5 through 21 are graphic plots of product properties comparing various process parameters for the improved process and lube products.

Preferred reactor systems are depicted schematically in Figures 1 and 2.

Detailed Description of the Invention

In the following description, units are metric unless otherwise indicated.

I. Feedstock to the Integrated Process - Overview

The hydrocarbon feedstock to the integrated process of this invention is a lube range feed with an initial boiling point and final boiling point selected to produce a lube stock of suitable lubricating characteristics. These feedstocks are predominantly hydrocarbons having a 10% distillation point greater than 345°C (653°F) and a viscosity of from about 3 to about 40 centistokes at 100°C as can be determined from Figure 3 or similar correlations. The feed is conventionally produced by the vacuum distillation of a fraction from a crude source of suitable type. Generally, the crude will be subjected to an atmospheric distillation and the atmospheric residuum (long resid) will be subjected to vacuum distillation to produce the initial unrefined lube stocks. The vacuum distillate stocks or "neutral" stocks and bright stocks from propane deasphalting the vacuum distillation bottoms are used to produce a range of viscosity products. Viscosities typically may be 4 centistokes at 100°C for a light neutral, about 12 centistokes at 100°C for a heavy neutral, and about 40 centistokes at 100°C for bright stock. In conventional solvent refining lube plants, the feedstocks are subjected to solvent extraction to improve their V.I. and other qualities by selective removal of the aromatics using a solvent which is selective for aromatics such as furfural, phenol, or N-methyl-pyrrolidone. For the invention it is necessary to subject the feed to hydrocracking prior to dewaxing and hydrofinishing in order to obtain the desired product characteristics.

The unrefined vacuum distillates and propane deasphalted (PDA) raffinates are refined by hydrocracking or severe hydrotreating to convert undesirable aromatic and heterocyclic compounds to more desirable naphthenes and paraffins. (See Example 3 infra). These refined waxy mixtures are low in sulfur and nitrogen contents and after distillation may be adjusted for viscosity as described earlier.

Integrated all-catalytic lubricant production processes employing hydrocracking and catalytic dewaxing are described in U.S. Patents Nos. 4,414,097 (Chester et al.), 4,283,271 (Garwood et al.), 4,283,272 (Garwood et al.), 4,383,913 (Powell et al.), 4,347,121 (Mayer et al.), 3,684,695 (Neel et al.) and 3,755,145 (Orkin).

II. Hydrocracking Step

A. Feed to Hydrotreating/Hydrocracking System

The hydrocracking process operates with a heavy hydrocarbon feedstock such as virgin light vacuum gas oil, heavy vacuum gas, and deasphalted raffinate, or combination of these, all boiling above about 340°C. Although these virgin oils are preferred, cracked stocks such as light and heavy coker gas oils and light and heavy FCC gas oils may be added in amounts not to exceed 20% because of their low hydrogen contents. (They are highly aromatic). Because lube oils are generally sold according to their viscosities and because hydrocracking reduces viscosity, the feedstock to the hydrocracker must preferably have a kinematic viscosity at 100°C, of 3 cS or greater. This means that the preferred boiling range is above 340°C (See Figure 3, infra which shows a correlation of 50% boiling points and viscosities for pure components and vacuum gas oils from Arab light crude). Feedstocks boiling below 340°C may be included in the hydrocracker feed, but their even lighter products will be removed in the separator 20. (See Figure 1.) These heavy oils comprise high molecular weight long chain paraffins and high molecular weight naphthenes and aromatics. The aromatics will include some fused ring aromatics which are detrimental to lube oil stability. During the processing, the fused ring aromatics and naphthenes are cracked by the acidic catalyst and the paraffinic cracking products, together with paraffinic components of the initial feedstock, undergo conversion to iso-paraffins with some cracking to lower molecular weight

materials. Hydrogenation of the polycyclic aromatics is catalyzed by the hydrogenation component and facilitates cracking of these compounds. Hydrogenation of unsaturated side chains on the monocyclic cracking residues of the original polycyclic compounds provides substituted monocyclic aromatics which are highly desirable end products. The heavy hydrocarbon oil feedstock will normally contain a substantial amount boiling above 340°C (644°F) and have a viscosity above 3cS at 100°C. It will normally have an initial boiling point above about 400°C (752°F) and more usually above about 450°C (842°F). The boiling range may be as broad as 340-700°C (644-1292°F). Oils with a narrower boiling range may, of course, be processed, for example, those with a boiling range of about 400 to 500°C (about 752°F to 932°F). Heavy gas oils are often of this kind as are cycle oils and other non-residual materials. Cycle oils from catalytic cracking operations (FCC) and coking operations are not particularly useful for producing lube oils because they are so highly unsaturated but they may be blended into the virgin oils described above as long as they meet the same boiling and viscosity requirements described for the virgin oils. It is advisable that the hydrocracker feed stock not contain more than 20% cracked stock. The hydrocracker feedstock must comprise 80% or higher virgin components.

A preliminary hydrotreating step using a conventional hydrotreating catalyst to remove nitrogen and sulfur and to saturate aromatics to naphthenes without substantial boiling range conversion will usually improve catalyst performance and permit lower temperatures, higher space velocities, lower pressures or combinations of these conditions to be employed. Suitable hydrotreating catalysts generally comprise a metal hydrogenation component, usually a Group VIB, or VIII metal as described above e.g. cobalt-molybdenum, nickel-molybdenum, on a substantially non-acidic porous support e.g. silica-alumina or alumina. These are listed in Table 1.

Table 1

Catalysts Suitable for Use in Preliminary Hydrotreating Step

Vendor	Catalyst	Type
UOP	HCH	NiMo/A1203
Crossfield	594	NiMo/A1203
Crossfield	504-K	NiMo/A1203
Criterion	HDN60	NiMo/A1203
Criterion	C-411	NiMo/A1203
Criterion	C-424	NiMo/A1203
Acreon	HR348	NiMo/A1203
Acreon	HR360	NiMo/A1203
Akzo	KF843	NiMo/A1203

II.B Description of the Preferred Embodiment

Figure 1 is a simplified illustration of the preferred reactor system for the fuels hydrocracker of this invention. A preliminary hydrotreating step using a conventional hydrotreating catalyst to remove nitrogen, sulfur, and oxygen, and to saturate olefins and aromatics without substantial boiling range conversion will usually improve the hydrocracking catalyst performance and permit higher space velocities, lower pressures, or combinations of these conditions to be employed. Suitable hydrotreating catalysts generally comprise a metal hydrogenation component, usually from Groups VIII and VIB, such as cobalt-molybdenum or nickel-molybdenum, on a low-acidity porous support such as silica-alumina or alumina. Appropriate commercial hydrotreating catalysts suitable for use in the instant invention include alumina supported nickel-molybdenum catalysts, such as UOP HCH, Crossfield 594, and Criterion HDN60, and USY supported nickel-molybdenum catalysts, such as UOP HC-24.

A vertical reactor shell 10 encloses and supports a stacked series of fixed porous solid beds of hydrotreating catalyst, as depicted by 12A through 12E. A chargestock 6

comprising vacuum gas oil, light cycle oil, deasphalted oil or any combination of these is combined with a hydrogen-rich gas 8 and introduced to the reactor 10 after undergoing appropriate heating means 9. The combined chargestock and hydrogen-rich gas flow downwardly through the catalyst beds. Although 5 beds are depicted in this example, there may be more beds or as few as two. Liquid distribution in each bed is achieved by any conventional technique, such as distributor trays 13A, B, C, D, E, which project the liquid uniformly onto the catalyst bed surfaces 12A, B, C, D, E. Typically the gas and liquid phases are introduced into the reactor at a desired inlet pressure and temperature. The gas and liquid temperature may be adjusted between catalyst beds by the addition of hydrogen-rich quench gas 14A, B, C, D or alternatively by heat exchange of the liquid in an external flow loop, thereby allowing independent control of the temperature in any catalyst bed. A static mixer 15A, B, C, D or other suitable contacting device may be used to mix the liquid and gas streams between catalyst zones, including quench gas, to obtain a homogeneous temperature.

The hydrotreater effluent 16 passes through heat exchangers (not shown), separators 18 and stripping or fractionation equipment 20 to separate a recycle gas stream 22 and light conversion products 24. These separations remove byproduct NH_3 and H_2S, which would otherwise poison the hydrocracking catalyst downstream. A purge gas stream 28 would typically be withdrawn from the recycle gas to remove light hydrocarbon products. Gas scrubbing facilities (not shown) would typically be used to remove NH_3 and H_2S from the recycle gas stream. Makeup hydrogen 26 is added to compensate for hydrogen consumed in the hydrotreating reactions and purged in the gas and liquid product streams 28, 24, and 30.

A vertical reactor shell 34 encloses and supports a stacked series of fixed porous solid beds of hydrocracking catalyst, as depicted by 36A through 36E. The

hydrocracking catalyst, which may be more than one catalyst, either admixed or in separate beds, is discussed infra. The hydrotreater bottoms product 30 is combined with a hydrogen-rich gas 32 and introduced to the hydrocracking reactor 34 after undergoing appropriate heating means 33. The combined chargestock and hydrogen-rich gas flow downwardly through the catalyst beds. Although 5 beds are depicted in this example, there may be more beds or as few as two. Liquid distribution in each bed is achieved by any conventional technique, such as distributor trays 37A, B, C, D, E, which project the liquid uniformly onto the catalyst bed surfaces 36A, B, C, D, E. Typically the gas and liquid phases are introduced into the reactor at a desired inlet pressure and temperature. The gas and liquid temperature may be adjusted between catalyst beds by the addition of hydrogen-rich quench gas 38A, B, C, D or alternatively by heat exchange of the liquid in an external flow loop, thereby allowing independent control of the temperature in any catalyst bed. A static mixer 39A, B, C, D or other suitable contacting device may be used to mix the liquid and gas streams between catalyst zones, including quench gas, to obtain a homogeneous temperature.

The hydrocracker effluent 38 passes through heat exchangers (not shown), separators 40 and fractionation equipment 42 to separate a recycle gas stream 44 and converted hydrocracked fractions 46. A purge gas stream 50 would typically be withdrawn from the recycle gas to remove light hydrocarbon products. Gas scrubbing facilities (not shown) would typically be used to remove NH_3 and H_2S from the recycle gas stream. Makeup hydrogen 48 is added to compensate for hydrogen consumed in the hydrocracking reactions and purged in the gas and liquid product streams 50 and 46. The unconverted bottoms product 52, proceeds to the lube vacuum distillation unit 54, one of the novel features of the instant invention. This additional distillation step enables the production of various narrow lube fractions 56, 58, 60, 62, 64 of specific viscosity

(e.g., 60N, 100N, 150N) and volatility. Low volatility lube stocks with a VI of at least 115 can be produced. Although five lube cuts are shown, there may be more or as few as two. These lube fractions, are passed from the vacuum distillation unit 54 to the catalytic dewaxing process as illustrated in Figure 2.

In some instances it may be desirable to recycle some of the unconverted hydrocracker bottoms product 52 or unused fractions of this stream from the vacuum distillation unit 56, 58, 60, 62, 64 back to the hydrocracker 34. This is shown as stream 66. Alternatively, it may be desirable to send these unconverted hydrocracker bottoms streams to a second hydrocracker, to an FCC unit, or to fuel.

Tables 3 and 4 (see Example 1, infra) illustrate how the lube product from a hydrocracker can be tailored by the addition of a lube vacuum distillation unit, as described in the instant invention.

II.C Hydrocracking Catalyst

The catalyst used in the present hydrocracking process may be a conventional hydrocracking catalyst which employs an acidic large pore size zeolite within the porous support material with an added metal hydrogenation/dehydrogenation function. Specific commercial hydrocracking catalysts, which may be used include UOP HC-22, and UOP HC-24. These are NiMo catalysts on a support of USY. ICR209, a Chevron catalyst which comprises Pd on a USY support, may also be employed. Table 2 lists suitable hydrocracking catalysts. The acidic functionality in the hydrocracking catalyst is provided either by a large pore, amorphous material such as alumina, silica-alumina or silica or by a large pore size crystalline material, preferably a large pore size aluminosilicate zeolite such as zeolite X, Y, ZSM-3, ZSM-18, ZSM-20 or zeolite beta. The zeolites may be used in various cationic and other forms, preferably forms of higher stability so as to resist degradation and consequent

loss of acidic functionality under the influence of the hydrothermal conditions encountered during the hydrocracking. Thus, forms of enhanced stability such as the rare earth exchanged large pore zeolites, e.g. REX and REY are preferred, as well as the so-called ultra stable zeolite Y (USY) and high silica zeolites such as dealuminized Y or dealuminized mordenite.

Zeolite ZSM-3 is disclosed in U.S. Pat. No. 3,415,736, zeolite ZSM-18 in U.S. Pat. No. 3,950,496 and zeolite ZSM-20 in U.S. Pat. No. 3,972,983, to which reference is made for a description of these zeolites, their properties and preparations. Zeolite USY is disclosed in U.S. Pat. No. 3,293,192 and RE-USY is disclosed in U.S. Pat. No. 4,415,438. Hydrocracking catalysts comprising zeolite beta are described in EP94827 and U.S. Pat. No. 4,820,402, to which reference is made for a description of such catalysts.

The catalysts preferably include a binder such as silica, silica/alumina or alumina or other metal oxides e.g. magnesia, titania, and the ratio of binder to zeolite will typically vary from 10:90 to 90:10, more commonly from about 30:70 to about 70:30 (by weight).

Table 2

Catalysts Suitable for Use in Hydrocracking Step Prior to Dewaxing

Vendor	Catalyst	Type
UOP	HC-24	NiMo/USY
Chevron	ICR209	Pd/USY
Acreon	HYC 632	NiMo/Zeolite
Acreon	HYC 642	NiMo/Zeolite
Acreon	HYC 652	NiMo/Zeolite
Akzo	KC-2000	NiMo/Zeolite
Akzo	KC-2100	Pd/Zeolite
Criterion	Z-703	NiW/Zeolite
Criterion	Z-753	NiW/Zeolite
Criterion	Z-763	NiW/Zeolite

II.D Hydrocracking Process Considerations

This hydrocracking Process is carried out under conditions similar to those used for conventional hydrocracking. Process temperatures of about 260° to 480°C (500°F to 896°F) may conveniently be used although temperatures above about 445°C (833°F) will normally not be employed since the thermodynamics of the hydrocracking reactions becomes unfavorable at temperatures above this point. Generally, temperatures of about 315°C to 425°C (599° to 797°F) will be employed. Total pressure is usually in the range of 1200 to 3000 psi (8274 to 20,685 kPa) and the higher pressures within this range over 1800 psi (12,600 kPa) will normally be preferred. The process is operated in the presence of hydrogen and hydrogen partial pressures will normally be at least 1200 psig (8274 kPa). The ratio of hydrogen to the hydrocarbon feedstock (hydrogen circulation rate) will normally be from 2000 to 5000 SCF/Bbl. (about 18 to 980 $n.1.1^{-1}$). The space velocity of the feedstock will normally be from 0.1 to 10 LHSV (hr^{-1}), preferably 0.5 to 5 LHSV. At low conversions, the n-paraffins in the feedstock will be isomerized to iso-paraffins but at higher conversion under more severe conditions the iso-paraffins will be converted to lighter materials.

The conversion may be carried out by contacting the feedstock with a fixed stationary bed of catalyst. A simple configuration is a trickle-bed operation in which the feed is allowed to trickle through a stationary fixed bed (Figure 1 illustrates this). With such a configuration, it is desirable to initiate the reaction with fresh catalyst at a moderate temperature which is of course raised as the catalyst ages, in order to maintain catalytic activity. The hydrocracking catalyst may be regenerated by contact at elevated temperature with hydrogen gas, for example, or by burning in the presence of a mixture of air, nitrogen and flue gas.

III. Catalytic Dewaxing Process (or Hydrodewaxing or Hydroisomerization Process)

Figure 2 illustrates a specific embodiment of the instant invention and is not intended to be limiting. A vertical reactor shell 10 encloses and supports a stacked series of fixed porous solid beds of dewaxing catalyst, as depicted by 12A through 12C. A chargestock 6 comprising wax-containing liquid oil is combined with a hydrogen-rich gas 8 and introduced to the reactor 10 after undergoing appropriate heating means 9. The combined chargestock and hydrogen-rich gas flow downwardly through the catalyst beds. Although 3 beds are depicted in this example, there may be more beds or as few as two. Liquid distribution is achieved by any conventional technique, such as distributor trays 13A, B, C, which project the liquid uniformly onto the catalyst bed surfaces 12A, B, C. Typically the gas and liquid phases are introduced into the reactor at a desired inlet pressure and temperature. The gas and liquid temperature may be adjusted between catalyst beds by the addition of hydrogen-rich quench gas 14A, B or alternatively by heat exchange of the liquid in an external flow loop, thereby allowing independent control of the temperature in any catalyst bed. A static mixer 15A, B or other suitable contacting device may be used to mix the liquid and gas streams between catalyst zones, including quench gas, to obtain a homogeneous temperature.

The hydrodewaxing reactor effluent 24 is heated or cooled, as necessary via heat exchange or furnace 25 and cascaded directly into the hydrofinishing reactor 30. A vertical reactor shell 30 encloses and supports a stacked series of fixed porous solid beds of hydrofinishing catalyst, as depicted by 32A through 32C. The liquid and gas flow downwardly through the catalyst beds. Although 3 beds are depicted in this example, there may be more beds or as few as two. Liquid distribution is achieved by any conventional technique, such as distributor trays 33A, B,

C, which project the liquid uniformly onto the catalyst bed surfaces 32A, B, C. Typically the gas and liquid phases are introduced into the reactor at a desired inlet pressure and temperature. The gas and liquid temperature may be adjusted between catalyst beds by the addition of hydrogen-rich quench gas 34A, B or alternatively by heat exchange of the liquid in an external flow loop, thereby allowing independent control of the temperature in any catalyst bed. A static mixer 35A, B or other suitable contacting device may be used to mix the liquid and gas streams between catalyst zones, including quench gas, to obtain a homogeneous temperature.

The hydrofinisher effluent 36 passes through heat exchangers (not shown), separators 40 and fractionation equipment 42 to separate a recycle gas stream 44, converted fractions 46, and a finished lube base stock 48. A purge gas stream 50 would typically be withdrawn from the recycle gas to remove light hydrocarbon products. Gas scrubbing facilities (not shown) would typically be used to remove NH_3 and H_2S from the recycle gas stream. Makeup hydrogen 52 is added to compensate for hydrogen consumed in the hydrodewaxing and hydrotreating reactions and purged in the gas and liquid product streams 50 and 46.

The continuous multi-stage reactor system has been described for contacting gas and liquid phases with a series of porous catalyst beds; however, it may be desired to have other reactor configurations with 2-5 beds. The catalyst composition may be the same in all beds of each reactor; however, it is within the inventive concept to have different catalysts and reaction conditions in the separated beds. Design and operation can be adapted to particular processing needs according to sound chemical engineering practices.

The present technique is adaptable to a variety of catalytic dewaxing operations, particularly for treatment of lubricant-range heavy oils with hydrogen-containing gas at elevated temperature. Industrial processes employing

hydrogen, especially petroleum refining, employ recycled impure gas containing 10 to 30 mole % or more of impurities, usually light hydrocarbons and nitrogen. Such gases are available and useful herein, especially for high temperature hydrodewaxing at elevated pressure.

Advantageously, the catalyst bed has a void volume fraction greater than 0.25. Void fractions from 0.3 to 0.5 can be achieved using loosely packed polylobal or cylindrical extrudates, spheres or pellets providing adequate liquid flow rate component for uniformly wetting catalyst to enhance mass transfer and catalytic phenomena. Catalyst bed depths may range from 2 to 6 meters.

In the present process, a waxy lube feedstock, typically a 321°C+ (about 610°F+) feedstock is subjected to an intermediate pore size molecular sieve catalyst having dewaxing and/or isomerization or hydroisomerization functions in the presence of hydrogen to produce a dewaxed lube boiling range product of low pour point (ASTM D-97 or equivalent method such as Autopour). For typical waxy feedstock the hydrogen feedrate at the top of the dewaxing reactor is about 267-534 n.l.l.-1 (1500-3000 SCF/BBL). In order to improve the stability of the dewaxed lube boiling range materials in the dewaxed effluent, a hydrofinishing step is generally carried out.

Hydrodewaxing Process Considerations

In general terms, when ZSM-5 is the active component in the catalyst, the catalytic dewaxing process step is operated under conditions of elevated temperature, usually ranging from about 205° to 400°C (401° to 752°F), preferably from 235° to 385°C (455° to 725°F), depending on the dewaxing severity necessary to achieve the target pour point for the product. When other less active catalysts are used, the temperature may be 25 to 50°C higher than for ZSM-5.

As the target pour point for a product is decreased the severity of the dewaxing process is increased by raising

the reactor temperature so as to effect an increasingly greater conversion of normal paraffins, so that lube yield will generally decrease with decreasing product pour point as successively greater amounts of the normal paraffins (wax) in the feed are converted by selective cracking by the dewaxing catalyst to lighter products boiling outside the lube boiling range. The V.I. of the product will also decrease as pour point is lowered because the high V.I. normal paraffins and slightly branded isoparaffins are progressively converted.

In addition, the dewaxing temperature is increased during each dewaxing cycle to compensate for decreasing catalyst activity due to catalyst aging. The dewaxing cycle will normally be terminated when a temperature of about 400°C (about 750°F), but preferably about 385°C (725°F) is reached since viscosity and product stability are adversely affected at higher temperatures. When ZSM-5 is the active catalytic ingredient with less active catalysts, these temperatures may be 25 to 50°C higher.

Hydrogen promotes extended catalyst life by a reduction in the rate of coke laydown on the dewaxing catalyst. ("Coke" is a highly carbonaceous hydrocarbon which tends to accumulate on the catalyst during the dewaxing process.) The process is therefore carried out in the presence of hydrogen, typically at about 2758 to 20,685 kPa hydrogen partial pressure (400 to 3000 psia), preferably between 9653 to 17238 kPa (1400 to 2500 psi) more preferably between 1600 to 2200 psi (11032 to 15169 kPa) although higher pressures can be employed. Hydrogen circulation rate is typically 180 to 710, usually 355 to 535 n.1.1.$^{-1}$ (1000 to 4000 SCF/bbl, usually 2000 to 3000 SCF/bbl) of liquid feed at the reactor inlet additional H_2 may be added at the quench points. Space velocity will vary according to the chargestock and the severity needed to achieve the target pour point but is typically in the range of 0.25 to 5 LHSV (hr^{-1}), preferably 0.5 to 3 LHSV for all catalysts.

Hydrodewaxing Catalysts

Recent developments in zeolite technology have provided a group of constrained medium pore siliceous materials having similar pore geometry. The preferred hydrodewaxing catalyst comprises a porous acid molecular sieve having pores comprised of 10 oxygen atoms alternating with predominantly silicon atoms, such as aluminosilicate zeolite. Most prominent among these intermediate pore size zeolites are ZSM-5, ZSM-23, ZSM-35 and ZSM-48 which are usually synthesized with Bronsted acid active sites by incorporating a tetrahedrally coordinated metal, such as Al, Ga, or Fe, within the zeolitic framework. Medium pore molecular sieves having pore dimensions about 3.9 to 6.3 Angstroms are favored for shape selective acid catalysis; however, the advantages of medium pore structures may be utilized by employing highly siliceous materials or crystalline molecular sieve having one or more tetrahedral species having varying degrees of acidity. These shape selective materials have at least one channel with pores formed by ten-member rings containing ten oxygen atoms alternating with silicon and/or metal atoms.

The catalysts which have been proposed for shape selective catalytic dewaxing processes have usually comprised molecular sieves which have a pore size which admits the straight chain, waxy n-paraffins either alone or with only slightly branched chain paraffins but which exclude more highly branched materials and cycloaliphatics. Representative of the medium pore molecular sieves are ZSM-5 (US Pat. No. 3,702,886), ZSM-11 (US Pat. No. 3,709,979), ZSM-22, ZSM-23 (US Pat. No. 4,076,842), ZSM-35 (US Pat. No. 4,016,245), ZSM-48 (US Pat. No. 4,375,573), ZSM-57, and MCM-22 (US Pat. No. 4,954,325) and SAPO-11 (U.S. Pat. No. 4,859,311). ZSM-24 is a synthetic ferrierite. (See Fig. 4) The disclosures of these patents are herein incorporated by reference.

Molecular sieves offer advantages in catalytic dewaxing over noncrystalline catalysts. Molecular sieves are

broadly classed into small, medium (or intermediate), and large pore materials as shown in Figure 4. The pore size is fixed by a ring of oxygen atoms. Small pore zeolites have eight-membered ring openings, medium have ten-membered systems and large have twelve-membered systems. Catalytic dewaxing performance can also be affected by the catalyst's pore structure, whether it has uni- or bi-dimensional channels, and the nature of its channel intersections. Severely constrained, small pore zeolites are ineffective in lube oil dewaxing because they allow only small, normal paraffins to penetrate the pore channel. In comparison, large pore zeolites permit non-selective cracking of some desirable lube components resulting in lower yields than those from medium pore zeolites.

HZSM-5 is one of a number of medium pore size zeolites which are capable of shape-selective dewaxing. Other examples include ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48 and ZSM-57. The pore structure of ZSM-5 provides a balance of reactant shape selectivity, reduced coking tendency and exclusion of bulky nitrogen-containing catalyst poisons. HZSM-5, Pt/ZSM-23, Pd/ZSM-23, Pt/ZSM-48 and Pt/SAPO-11 with appropriately adjusted physicochemical properties are preferred in the instant invention because their channel systems and pore dimensions enable effective de-waxing of fuels hydrocracker bottoms.

Suitable molecular sieves having a coordinated metal oxide to silica molar ratio of 20:1 to 200:1, or higher may be used. With HZSM-5, for example, it is advantageous to employ conventional aluminosilicate ZSM-5 having a silica:alumina molar ratio of about 25:1 to 70:1 although ratios above 70:1 may be used. A typical zeolite catalyst component having Bronsted acid sites may consist essentially of crystalline aluminosilicate having the structure of ZSM-5 zeolite with 5 to 95 wt.% silica, clay and/or alumina binder. It is understood that other medium pore acidic molecular sieves, such as salicylate, silica-aluminophosphate (SAPO) materials may be employed as

catalysts, especially medium pore SAPO-11.

U.S. Pat. No. 4,908,120 (Bowes et al) discloses a catalytic process useful for feeds with high paraffin content or high nitrogen levels. The process employs a binder free zeolite dewaxing catalyst, preferably ZSM-5.

Medium pore zeolites are particularly useful in the process because of their regenerability, long life and stability under the extreme conditions of operation. Usually the zeolite crystals have a crystal size from about 0.01 to over 2 microns or more, with 0.02-1 micron being preferred. Although ZSM-5 (≥ 40 alpha) can be used in its metal-free form for selective cracking, in the case of the other medium pore acidic metallo-silicates described supra, it is necessary that they be modified with from 0.1 to 1.0 wt.% of a noble metal in order to be used as hydroisomerization dewaxing catalysts.

ZSM-5 is the only medium pore zeolite or medium pore acidic molecular sieves that is practical to use for commercial selective dewaxing without adding a noble metal. The noble metal is required with other medium pore molecular sieves in order to reduce catalyst aging rates to practical levels. The addition of a noble metal to ZSM-5, however, provides it with hydroisomerization activity that increases yields of dewaxed lube oils. It has been found that when noble metals are added to ZSM-23, ZSM-35, SAPO-11 and ZSM-5, the product yields and VI are generally higher for ZSM-23, ZSM-35 and SAPO-11 than for ZSM-5. The choice of which catalyst to use becomes one of economics.

Catalyst size can vary widely within the inventive concept, depending upon process conditions and reactor structure. Finished catalysts having an average maximum dimension of 1 to 5mm are preferred.

Catalytic Dewaxing Conditions

In most of the catalytic dewaxing examples herein the catalyst employed is 65 wt% ZSM-5 having an acid cracking (alpha) value of 105, and formed as 1.6 mm diameter

extrudate; however, alpha values from about 1 to about 300 may be used. Reactor configuration is an important consideration in the design of a continuously operating system. In its simplest form, a vertical pressure vessel is provided with a series (at least 2) of stacked catalyst beds of uniform cross-section. A typical vertical reactor having a total catalyst bed length to average width (L/D aspect) ratio of about 1:1 to 20:1 is preferred. Stacked series of beds may be retained within the same reactor shell; however, similar results can be achieved using separate side-by-side reactor vessels. Reactors of uniform horizontal cross section are preferred; however, non-uniform configurations may also be employed, with appropriate adjustments in the bed flux rate and corresponding recycle rates.

The invention is particularly useful in catalytic hydrodewaxing of heavy petroleum gas oil lubricant feedstock boiling above 315°C (599°F). The catalytic dewaxing treatment may be performed at an hourly liquid space velocity not greater than 5 hr^{-1}, preferably about 0.5-3 hr^{-1}, over randomly packed beds of extrudate catalyst of the medium pore type molecular sieve catalyst. The hydrocarbon feedstock to the catalytic dewaxer has a viscosity of 3 to 12 cSt at 100°C. Advantageously, the liquid flux rate for total feed rate (including optional liquid recycle) is maintained in the range of 2441-17088, preferably 4882-14647 $kg/m^2/hr$ (500-3500 $pounds/ft^2$-hr, preferably 1000-3000 $pounds/ft^2$-hr.). The reactant gas is fed at a uniform volumetric rate per barrel of oil.

IV. Hydrofinishing Following Catalytic Dewaxing

In order to improve the quality of the dewaxed lube products, a hydrofinishing step (see Figure 2) follows catalytic dewaxing in order to saturate lube range olefins as well as to remove heteroatoms, color bodies and, if the hydrofinishing pressure is high enough, to effect saturation of residual aromatics. The post-dewaxing

hydrofinishing is usually carried out in cascade with the dewaxing step. Generally, at start-of-cycle, the hydrofinishing will be carried out at temperatures from about 230°C to 330°C, preferably 246-274°C and most preferably 260-302°C (450°F to 625°F, 475°F to 600°F and most preferably 500-575°F). Total pressures are typically from 9653 to 20,685 kPa (about 1400 to 3000 psi). Liquid hourly space velocity in the hydrotreater is typically from 0.1 to 5 LHSV (hr^{-1}), preferably 0.5 to 3 hr^{-1}.

Processes employing sequential lube catalytic dewaxing-hydrofinishing are described in U.S. Patents Nos. 4,181,598, 4,137,148 and 3,894,938. A process employing a reactor with alternating dewaxing-hydrofinishing beds is disclosed in U.S. Patent No. 4,597,854. Reference is made to these patents for details of such processes. The hydrofinishing step following the dewaxing step improves product quality without significantly affecting its pour point. The metal function on the hydrofinishing catalyst is effective in saturating aromatic components. Thus, a hydrofinishing (HDF) catalyst with a strong desulfurization/hydrogenation function that a noble metal, nickel-tungsten or nickel-molybdenum can provide, will be more effective than a catalyst comprising a weaker metal function such as molybdenum alone. The preferred hydrofinishing catalysts for aromatics saturation will comprise at least one metal having relatively strong hydrogenation function on a porous support. Because the desired hydrogenation reactions require little acidic functionality and because no conversion to lower boiling products is desired in this step, the support of the hydrofinishing catalyst is of low acidity. Typical support materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina of low-acidic character. The metal content of the catalyst is often as high as about 20 weight percent for non-noble metals. Noble metals are usually present in amounts no greater than 1.0 wt.%. Hydrofinishing catalysts of this type are

readily available from catalyst suppliers. The nickel-tungsten catalysts may be fluorided.

Control of the reaction parameters of the hydrofinishing step offers a useful way of varying the stability of the products. Using a combination of Periodic Group VIIIA and VIA (IUPAC Periodic Table) metals, such as Ni/W, hydrofinishing catalyst temperatures of about 230°-300°C (446°-572°F) will minimize single-ring aromatics and polynuclear aromatics. They will also provide products having good oxidative stability, UV light stability, and thermal stability. Space velocity in the hydrofinisher also offers a potential for aromatics saturation control with the lower velocities effecting greater aromatics saturation. The hydrofinished product preferably contains not more than 10 wt% aromatics.

Examples

The following examples are intended to be descriptive only and are in no way to be considered as limiting:

Example 1

Table 3 provides an analysis of an atmospheric tower bottoms product from a commercial two stage hydrocracker. Such a hydrocracker possesses a hydrotreater reactor and a hydrocracking reactor, but does not employ the vacuum distillation unit as described in the hydrocracking unit of the instant invention. The product is roughly a 330-538°C (625-1000°F) cut and is very low in heteroatom and aromatic content, particularly nitrogen. The hydrocracking catalyst employed was fresh. A full range analysis of the drum of the atmospheric tower bottoms as received is reported in the "total bottoms" column. The bottoms were broken down into five equal volume cuts and analyzed for key properties. These analyses are also provided in Table 3.

After the hydrodewaxing process, which includes catalytic dewaxing, hydrofinishing, and distillation, the final product must possess the following characteristics:

Viscosity Index $\geq$ 115
NOACK > 6 $\leq$ 20
Viscosity (4-5cSt at 100°C)
Color $\geq$ 20
Pour Point $\leq$ -4°C (25°F)
Aromatics $\leq$ 5 wt%
Color stable in sunlight

In order to obtain a final product with these characteristics, it is desirable to begin with a chargestock with as high a VI and as low a NOACK (or as high a flash point) as possible. The hydrodewaxing procedure lowers pour point. In Table 3, the more volatile fractions had lower pour points and the heavier, less volatile fractions had higher VI. The most volatile fraction, distilled at 0-20% had a low viscosity (2.77 centistokes at 100°C) and a VI below 115 and is therefore unsuitable for use.

It is desirable to obtain chargestock with characteristics in an acceptable range in order to attain the above product properties. In the instant invention, a vacuum distillation step is employed. As Table 4 illustrates, even the lightest, most volatile fraction of the hydrocracked and vacuum distilled bottoms product is suitable for use, having a VI greater than 115 and a viscosity greater than 4 centistokes at 100°C.

Table 3

Commercial Hydrocracker Atmospheric Bottoms

Distillation into 5 Equal-Volume Cuts

	Total Bottoms	0-20%	20-40%	40-60%	60-80%	80-100%
Yields on Dist.						
wt.%		19.4	19.0	18.7	19.9	23.1
vol%		19.5	19.1	18.6	19.8	22.9
Gravity, °API	38.4	39.4	39.5	37.7	37.8	37.2
Sp.Gr.60°F/60°F	0.8329	0.8280	0.8275	0.8363	0.8358	0.8388
Pour Point, °C (°F)	38(100)	16(60)	24(75)	32(90)	38(100)	49(120)
ASTM Color	<0.5					
COC Flash Point,°F	216.11(421)					
KV @ 40°C, cSt	19.33	10.23	13.72	17.34	--	--
KV @ 100°C, cSt	4.370	2.770	3.456	4.144	4.972	7.365
KV @ 300°C, cSt	2.285	1.521	1.824	2.062	2.460	3.278
SUS @ 38°C (100°F)	101	62	76	92	113	216
VI	141	114	132	147	--	--

Table 4

Vacuum Distillation Bottoms of Fuels Hydrocrackate
Distillation into 5 Equal-Volume Cuts

	Vacuum Distillation Bottoms	0-20%	20-40%	40-60%	60-80%	80-100%
Yields on Dist.						
wt.%		19.1	18.7	18.7	18.9	24.5
vol%		19.2	18.7	18.7	18.7	24.1
Gravity, °API	35.6	35.9	35.5	34.9	34.1	32.9
Sp.Gr.60°F/60°F	0.8468	0.8453	0.8473	0.8504	0.8545	0.8607
Pour Point, °C(°F)	43(110)	27(80)	29(85)	29(85)	29(85)	38(100)
ASTM Color	3.5					
COC Flash Point,°F	260°C(500)					
KV @ 40°C, cSt	--	23.76	--	--	--	--
KV @ 100°C, cSt	7.115	4.898	5.505	6.354	7.480	10.42
KV @ 300°C, cSt	3.308	2.373	2.626	2.933	3.359	4.308
SUS @ 38°C(100°F)	182	123	137	170	212	364
VI	--	133	--	--	--	--

Example 2

Figure 5 illustrates the relationship of Viscosity Index v. Hydrogen content for lube oils having a pour point of -7°C wherein the oils have been refined either by solvent refining or by hydrocracking. Each of the various waxy stocks compared was solvent dewaxed to a -7°C pour point. As the weight percent hydrogen present in a lubricant base stock increases, the VI, viscosity index, improves. The VI improves somewhat more for hydrocracked stocks than for solvent refined stocks. The empty circles represent lubestocks obtained by lubes hydrocracking, distillation and solvent dewaxing without further treatment. Circles containing crossed lines represent lubestocks refined by fuels hydrocracking, distillation and solvent dewaxing. Squares represent lubestocks that were solvent refined and solvent dewaxed. Upright triangles represent vacuum distillates obtained from paraffin crudes. Inverted triangles represent vacuum distillates obtained from naphthenic crudes.

It is apparent that fuels hydrocracking of vacuum gas oils will provide lubestocks of higher VI than lubes hydrocracking or solvent refining because fuels hydrocracking is more severe than lubes hydrocracking. In the instant invention, dewaxed lubestocks must have a VI of at least 115. From Figure 5, the dewaxed oil product must have a hydrogen content of at least about 14.1 wt% in order to obtain a VI of 115. Because dewaxing lowers hydrogen content the waxy oil must be about 0.2 to 0.5 wt% higher in hydrogen content than the dewaxed oil. Therefore, a critical feature of this invention is that the hydrocracker provide a vacuum distillation product having at least 14.3 wt% hydrogen. PONA analysis of these hydrocracked lubestocks on Figure 5 demonstrated that they possess wide variations in composition, some having a high paraffinic content and others having a high naphthenic content, others being in between. An infinite variety of compositions is therefore possible at any VI level and the variation can be

described by a range of hydrogen contents for any VI level. The hydrogen content of 150 isoparaffins ranges from 15.1 % to 14.6 % for carbon numbers ranging from C_{17} to C_{55}, respectively. For alkylcyclohexanes it is constant at 14.37% and for alkylbenzenes the range is 12.4 to 13.69 %. From this it follows that the dewaxed oil product must be rich in high hydrogen content isoparaffins and alkylcyclohexanes. A fuels hydrocracker, that is, a hydrocracker that operates in excess of 40% conversion to 345°C minus light products, can produce a 345°C plus product having the appropriate hydrogen content to provide a dewaxed oil having a viscosity index of 115.

Example 3

Figure 6 (parts a, b, and c) is a demonstration of lubes hydrocracking and fuels hydrocracking for a heavy vacuum gas oil derived from Statfjord crude oil. The heavy vacuum gas oil was hydrocracked in a pilot plant at various conversions and the hydrocrackate was distilled to remove all of the 345°C (653°F) materials. The waxy 345°C plus oils were then solvent dewaxed to -18°C (0°F) pour point and the viscosities and VI's were determined. The conversion range from 10 to about 30% is referred to as the lubes hydrocracking range and the conversion level from 30% and higher is referred to as the fuels hydrocracking range. It is obvious that to attain a dewaxed product having a VI of 115 hydrocracking conversion of about 35% is required. The degree of conversion required is dependent upon the viscosity of the feed to the hydrocracker. Figure 6 also demonstrates how viscosity is reduced as hydrocracking proceeds. This is why fuels hydrocrackers are limited to making products in the low viscosity range, such as 60 to 250 SSU at 100°F, or 3-6 centistokes at 100°C. Figure 6 also shows that 345°C$^+$ yields are low in fuels hydrocrackers.

The data in Examples 4 to 12 was obtained from a two reactor process for catalytic dewaxing and hydrotreating.

(See Example 5 for detailed discussion.) The first reactor contained a proprietary hydrodewaxing catalyst, HZSM-5.

The same hydrodewaxing catalyst was used for both high and low pressure operation. In the second reactor a commercial hydrofinishing catalyst was employed. In low pressure (2.86×10^3-4.2×10^3 kPa) operation, the hydrofinishing catalyst is designed only for olefin saturation. Some level of aromatics saturation is necessary for good oxidative and UV light stability, however. A hydrofinishing catalyst which operates at high pressure (1.73×10^4 kPa) was used for aromatics saturation. The hydrofinishing catalyst employed at low pressure was evaluated at 1.53×10^4 kPa in order to provide a comparison.

Example 4

The NOACK volatility test (see Figures 7 and 8) which was done on the neat (unadditized) base stocks, follows CEC L-40-T-87 "Evaporation Loss of Lubricating Oils" using the NOACK Evaporative Tester. In summary, the method measures the wt% evaporative loss of a sample held at 250°C (482°F) under a constant stream of air for a period of 60 minutes.

NOACK volatilities of the base stocks produced by high and low pressure catalytic dewaxing followed by hydrofinishing are shown on Figure 7. In general, NOACK volatility can be correlated with the percent off at 399°C (750°F) in D2887 simulated distillation (see Figure 7 and Table 5). For these products there is also good correlation between NOACK and the 10% point. (see Figure 8).

Flash point and Noack behave in an opposite fashion when related to 5% or 10% boiling points respectively. Figure 9 provides a correlation of flash point and 5% boiling point.

Table 5

Comparison of Products Obtained Employing High Pressure HDF v. Standard HDF

	Type HDF Cat		Aromatics Saturation Catalyst		Standard Olefin Saturation		Catalyst Hydrofinishing	
Conditions								
Pressure, kPa(psig) (100% H_2)	1.73x10⁴ kPa (2500)	1.73x10⁴ kPa (2500)	1.73x10⁴ kPa (2500)	1.73x10⁴ kPa (2500)	2.86x10³kPa (400)	2.86x10³kPa (400)	2.86x10³kPa (400)	1.53x10⁴kPa (2200)
HDT Temp, °F	329 (625)	302 (575)	274 (525)	232 (450)	241 (465)	260 (500)	288 (550)	260 (500)
Neat (Unadditized) Oil								
NOACK Volatility, wt%	23.8	18.8	17.9	20.3	18.6	17.7	19.5	18.0
SAB Color	28	28	29	29	1.0	1.5	-16	9
Light Stability, Days to Haze/Ppt	42+	42+	42+	42+	<4	<4	<4	<4
Sim Dist, % off at 399°C (750°F)	26.3	21.0	20.8	20.7	22.3	21.6	24.6	24.6
UV Absorptivity, L/g-cm								
226 nm	0.0113	0. 00415	0.00255	0.0281	0.923	0.766	0.726	0.324
254 nm	0.000740	0.000379	0.000219	0.00119	0.13 3	0.122	0.129	0.0223
275 nm	0.00120	0.000461	0.000283	0.00250	0.161	0.142	0.158	0.0372
325 nm	0.000460	0.000063	<0.000100	<0.000100	0.0287	0.0341	0.0467	0.00336
400 nm	0.000006	0.000003	<0.000100	<0.000100	0.00275	0.00386	0.00513	<0.000100
Oil + 0.3% Irganox ML 820								
RBOT Oxidation Test Minutes to 25 psi drop	580	500	565	565	472	510	640	560

Example 5

Both catalyst systems (high pressure catalytic dewaxing + Arosat HDF catalyst (fluoridated NiW/Al_2O_3) and low pressure catalytic dewaxing + HDF catalyst (Mo/Al_2O_3) easily met specification pour point and produced similar lube yields and viscosities with hydrocracked low aromatic, low nitrogen feedstock. General characteristics are summarized below.

Operation at 1.73×10^4 kPa (vs. 2.86×10^3 kPa) [(2500 psig vs. 400 psig)] reduces dewaxing catalyst aging from 2.3 to 0.2°F/day, greatly extending potential cycle length and improving unit stream factor. Pour point reduction is twice as responsive to catalytic dewaxing temperature changes at the high pressure, which could facilitate production of very low pour point base stocks, if desired. (See Figure 10)

Lube yields and VI's are relatively insensitive to pressure (see Figure 11), producing 67-72 wt.% yield of 121 VI, 116 SUS base stock at -15°C pour point (versus 82 wt.%, 129 VI, 107 SUS with solvent dewaxing on a dry wax basis).

Standard low pressure catalytic dewaxing allowed little adjustment in total aromatics levels as determined by UV absortivity at 226 nm (Figure 12). Use of an aromatics saturation catalyst at 1.73×10^4 kPa (2500 psig) allowed reduction of aromatics to equilibrium levels at 274°C (525°F) HDF temperature, as determined by UV absorptivities.

The low pressure program was run in a two-reactor pilot plant with online N_2 stripping capability. Reactor 1 was loaded with 225 cc of dewaxing catalyst, HZSM-5. Reactor 2 was loaded with 225 cc of hydrofinishing catalyst (Mo/Al_2O_3), which is designed for olefin saturation and low desulfurization (critical for maintaining oxidation stability of conventionally-refined lube base stocks). Both catalysts were 1/16" cylindrical extrudates and were commercially produced.

The low pressure work was done at 400 psig total

pressure using pure H_2 2.9 x 10^3 kPa (415 psi H_2 partial pressure) and 1 LHSV (each reactor), with 1.73 x 10^4 kPa (2500 scf/B) H_2 circulation. Three HDF temperatures (241°C, 274°C, and 288°C) were investigated at specification pour point (-15°C) to bracket an optimum treating severity for producing UV light-stable base stock.

High pressure catalytic dewaxing was performed in a two reactor pilot plant. Reactor 1 was loaded with 262 cc of dewaxing catalyst. This catalyst was the same dewaxing catalyst used in the standard pressure run. Reactor 2 was loaded with 62 cc of a commercial hydrofinishing catalyst with excellent aromatics saturation capabilities (Arosat). It is commercially available as a 1/16" quadrulobe extrudate.

The high pressure catalytic dewaxing was done at 1.73 x 10^4 kPa (2500 psig_ total pressure using pure H_2 1.74 x 10^4 kPa(H_2 partial pressure) and 1 LHSV (each reactor), with 445 n.l.l. (2500 Scf/B H_2 circulation). Four hydrofinishing temperatures (329°C, 302°C, 274°C and 232°C) were investigated at specification pour point (-15°C) to bracket an optimum treating severity for producing UV light-stable base stock. The data of Figure 12 clearly demonstrate that good aromatic saturation catalysts are needed in the hydrofinisher following the dewaxing reactor.

Example 6

SUNLIGHT STABILITY

Description of Method

In this test, the neat (unadditized) base stock is exposed to natural sunlight in a glass bottle and observed periodically for haze, precipitate, and color change. All samples were run simultaneously at the same location.

Results

Light stability of the high pressure catalytic dewaxed and hydrotreated base stocks is excellent when the aromatic saturation catalyst is used, with no precipitate after 42

days (see Figure 13). Products from low pressure catalytic dewaxing and hydrofinishing and also from solvent dewaxing have very poor light stability, deteriorating badly and about equally within 2-3 days. This would indicate that the light instability is not a result of anything occurring in the catalytic dewaxing step, but rather a result of unstable components in the hydrocracker bottoms. Such instability is generally associated with 3+ ring aromatics, which can be monitored by UV absorptivity at 325 nm. After absorption of light these compounds oxidize to produce free radical chain initiators, which subsequently react with other hydrocarbons to produce carboxylic acids. In low aromatic stocks such as these, solubility of these oxidation products is low and they precipitate out. The high pressure catalytically dewaxed and hydrofinished base stocks have UV absorptivities @ 325 nm that are several orders of magnitude below the other samples (see Figure 12 and Table 5). Note that the standard catalytic dewaxing hydrotreating catalyst, even at 1.53×10^4 kPa (2200 psig), is not well suited for removal of these unstable compounds. The light stability results of Figure 13 correlate with the UV results of Figure 14.

Example 7

The RBOT testing for oxidation stability (Rotary Bomb Oxidation of Turbine Oils) followed ASTM Method D2272. It was done using the base oils plus 0.3 wt.% Irganox ML820, which is a commercially available turbine oil additive package. In the test the sample is placed in a pressure bomb along with water and a copper catalyst coil. The bomb is pressured with oxygen to 620 kPa (90 psi), placed in a 150°C (302°F) bath, and rotated axially on an incline. The number of minutes required for the pressure to drop 172 kPa (25 psi) is reported; hence, higher results indicate superior oxidative stability. (See Table 5 and Figure 15).

Results

RBOT performance of high pressure catalytic dewaxing and low pressure catalytically dewaxed base stocks are comparable and good (see Figure 15). Solvent dewaxed oils from the same commercial feed also performed well, but were marginally lower on average. Relative to the catalytic dewaxed stocks, the solvent dewaxed hydrocracked samples were fair to poor, and showed a general trend of decreasing RBOT stability with increasing boiling range (25% bottoms vs. full range hydrocrackate) and increasing hydrocracker catalyst age End of Run (EOR) vs. Start of Run (SOR).

Example 8

Table 5 illustrates via extremely low UV absorptivities at 400 nm that polynuclear aromatics (PNA) are largely absent in lubes which have been treated with high pressure catalytic dewaxing followed by hydrofinishing. This correlates to the sunlight stability results on Figure 13.

Example 9

Dewaxing catalyst aging is significantly lower at 1.73 x 10^4 kPa (2500 psig) than it is at 2.8 x 10^3 kPa (400 psi). In addition, lube pour point is 2.3 times more responsive to dewaxing temperature changes at the higher pressure. These differences are attributed to lower rates of coke formation at the higher pressure.

Catalyst aging is depicted in Figure 10. Hydrodewaxing reactor (reactor 1) temperatures (actual and corrected to 5°F pour point) and pour point are shown versus days on stream. As is typical for low nitrogen stocks, aging rates are low relative to conventional, solvent-refined stocks.

High Pressure Catalytic Dewaxing Run

At 1.73 x 10^4 kPa (2500 psi) the catalyst lined out at

285°C (545°F) within the first two days on stream. Aging rate throughout the 36-day run was negligible. Consequently, extremely long cycle lengths are expected at 1.73×10^4 kPa (2500 psig).

Low Pressure Catalytic Dewaxing

At 2.8×10^3 kPa (400 psi), start of cycle temperature was about 530°F. Initial aging rate was -14°C (6.4°F/day) with a transition to a lower aging rate of -15°C (5.65°F/day). A pour point correction of 1.3°F pour/1°F change in HDW reactor temperature was effective for smoothing out the HDW reactor temperature data for pour points ranging from -30°C to 4°C (-22°F to +39°F).

After 29 days on stream, the pressure was increased to 2200 psi. Within 4 days, the catalyst recovered a substantial amount of its activity and the aging rate dropped to near-zero. This would suggest that the increased aging at 2.8×10^3 kPa (400 psig) resulted from higher coking rates, and some of this coke is easily hydrogenated or desorbed when the pressure is increased.

Example 10

In general, increasing catalytic dewaxing operating pressure tends to reduce distillate yield and correspondingly increase C_5 minus yields. Lube yield is relatively insensitive to pressure. Compared to solvent dewaxing (SDW) there is about a 10 wt.% debit in lube yield at -15°C (5°F) pour point, 70-72 wt.% for catalytic dewaxing with ZSM-5 catalyst vs. 82wt.% for solvent dewaxing (dry wax basis). However, it must be recognized that most solvent dewaxing units produce waxes that contain anywhere from 10-30% oil. Thus, actual solvent dewaxing yields are in the range of 74 to 80%.

Product yield distributions indicate that there is non-selective cracking occurring over the high activity, high pressure aromatic saturating catalyst at 329°C (625°F). Lube yield drops by 6 wt.%, as shown in Figure 16

(Lube Yield vs. Temperature) and Figure 17 (Viscosity vs. Hydrofinishing Severity at Constant Pour Point.) Most of this loss shows up as increased distillate yield. Sudden shifts in lube properties at 329°C (625°F) hydrotreating temperature also indicate non-selective cracking.

Throughout most of the hydrofinishing operating range explored, viscometric properties of both the low and high pressure catalytic dewaxing lube products are similar (Figure 18). At -15°C (5°F) pour point, viscosity is 4.6 cSt @ 100°C (116 SUS @ 100°F) and VI is 121. Solvent dewaxed oil viscosities are lower and VI's are higher, which is consistent with the differences in the way that the two processes achieve their goal.

It is apparent from the lube properties and yields discussed supra that there is non-selective cracking occurring over the Arosat hydrofinishing catalyst at 329°C (625°F). Lube viscosity drops off significantly, with a corresponding 3-5 number drop in VI.

(See Figure 18.)

Major differences between the properties of lubes made with low and high pressure catalytic dewaxing are a result of the degree of aromatics saturation in the hydrofinishing reactor -- a consequence of differences in (1) the type of hydrofinishing catalyst used and (2) the hydrogen pressure. These differences are even greater for aromatic feedstocks, e.g., deeper cut hydrocracked bottoms or end-of-cycle hydrocracked product.

Solvent dewaxing preferentially removes the heavier, higher-pour waxes, whereas catalytic dewaxing with ZSM-5 preferentially cracks the smaller, normal paraffins, which are also the highest VI components. As a result, catalytic dewaxed light neutral lube yields and VI's are lower. Low temperature viscometric performance of formulated catalytic dewaxed products are superior to solvent dewaxed oils of equivalent viscosity, however.

Example 11

UV absorptivity, as well as product appearance, was relied on for screening hydrofinishing reactor conditions during the pilot plant studies. Absorptivity at five wavelengths -- 226, 254, 275, 325, and 400 nm -- are used as qualitative indicators of the amount of aromatics, with 226 nm corresponding to total aromatics. Aromatics with three or more rings and four or more rings are indicated by absorptivities at 325 nm and 400 nm, respectively.

Lube aromatics are reduced dramatically over the Arosat HDF catalyst. The standard catalytic dewaxing HDF catalyst, which is designed for olefin saturation, is much less effective, even at 1.53 x 10^4 kPa (2200 psi) (see Figures 12 and 21). As seen in Figure 12, UV absorptivity at 226 nm (which correlates with total aromatics) goes through a minimum for the high pressure catalytic dewaxing near 274°C (525°F) -- marking the crossover from a kinetically-limited to an equilibrium-limited regime. This minimum should move toward higher HDF temperatures (and higher UV absorptivities) as feed aromatics increase. The standard catalytic dewaxing HDF catalyst is kinetically limited for saturating aromatics in the temperature range examined.

In general, saturation of polynuclear aromatics (400 nm) is relatively easy and the reaction is equilibrium limited in the normal range of hydrofinishing temperatures at high pressures, i.e., polynuclear aromatics decrease and then increase with hydrofinishing temperature. Higher hydrogen pressures shift the equilibrium to lower values.

Figures 19 and 20 show correlations of UV absorptivity v. aromatics content for two different hydrocrackates. One had low aromatics content and the other possessed high aromatics content. The data clearly demonstrates that high pressure and aromatic saturating hydrofinishing catalyst is better than low pressure hydrofinishing with standard hydrofinishing catalyst.

(See Table 6.)

Table 6

Comparison of Product Characteristics

HDW Temp, °C (°F)	HDF Temp, °C (°F)	Pressure, kPa	wt.% Aromatics in Lube (Chg = 14.3)	Lube Pour Point, °C (°F)	Lube Yield, wt.%	Fractional Yield of Aromatics (Lube Aromatics x Lube Yield)/ (Change Aromatics)
(316)	218	2.8×10^3 kPa (400)	15.3	-15 (5)	86	0.9
(335)	218	2.8 x 103 kPa (400)	20.7	-46 (-50)	76	1.1
(327)	218	1.53×10^4 kPa(2200)	1.7	-15 (5)	88	0.1

Example 13

Although many of the Examples above have employed HZSM-5 as the dewaxing catalyst, other catalysts, described supra, may also be used as dewaxing catalysts). This is illustrated on Figure 20 where the dewaxing catalyst was Pt on ZSM-23. Figure 18 shows that lube VI and yields obtained with Pt/ZSM-23 are about the same as or better than those obtained by solvent dewaxing.

Example 14

A number of medium pore molecular sieves were tested for their abilities to convert a normal paraffin that is representative of waxes in waxy light lube oil base stocks. The normal paraffin was n-hexadecane. The molecular sieves that were tested with this compound were ZSM-5, ZSM-23, ZSM-48 and SAPO-11. The acid activity of the catalysts, as measured by the "ALPHA" test, was varied for the molecular sieves either in the synthesis of the sieve or by steaming, which is known to reduce the activity of molecular sieves. A noble metal, namely platinum, was added to each catalyst made from the molecular sieves. The platinum concentration

was varied with some of the sieves. The following table lists the molecular sieves, their platinum contents and their "ALPHA" activities.

Table 7

Characteristics of Molecular Sieves

Molecular Sieve	Pt, Wt.%	"ALPHA" Activity	Temperature for 95% Conversion, at 0.4 LHSV °F
ZSM-23	0.5	30	547
ZSM-23	0.2	30	570
ZSM-23	0.5	1	603
ZSM-48	0.83	5	619
SAPO-11	0.7	9	600
ZSM-5	1.1	8	554
ZSM-5	0.4	1	603
ZSM-5	0.5	280	445 at 3.0 LHSV

All of these medium pore molecular sieves are capable of high conversions of a waxy compound such as n-hexadecane. The activity of the catalyst made from each molecular sieve can be significantly different depending upon the activity of the molecular sieve in the catalyst. The platinum content also affects the activity. Product selectivities are affected by the type of sieve, platinum content and "ALPHA" activity. Figure 21 is a plot of n-hexadecane conversion versus temperature requirements. Figure 22 is a plot of the yield of isomeric n-hexadecane conversion compounds having 16 carbon atoms versus hexadecane conversion. This figure shows that ZSM-48 and SAPO-11 give the best selectivity to isoparaffins in general. If a high alpha ZSM-5 is used, the selectivity is very low. However, Figure 23 shows that ZSM-23 gives the best selectivity to

the mono-branched isomers of normal hexadecane. This type of selectivity may be important in determining the VI of lubricant products. Thus, it is clear that the conversion of normal paraffins, or waxes, to isomeric compounds of the same molecular weight requires optimization of the noble metal content, and the acid activity and the pore structure of the molecular sieve for each molecular sieve used in making a finished catalyst.

Claims:

1. A process for the production of a dewaxed lubricant oil product, the process comprising at least one, hydrocracking zone, at least one hydrodewaxing zone and at least one hydrofinishing zone, the product possessing a pour point less than or equal to -4°C, a hydrogen content of at least 13.7 wt.%, a flash point of at least 200°C, a NOACK number of no more than 20, Saybolt color of at least 25, total aromatics of less than 10 wt. %, a viscosity of at least 3.0 cS at 100°C, a Viscosity Index (VI) of 115 or higher and excellent oxidative stability, UV light stability and thermal stability, the process comprising the following steps:

(a) hydrocracking feedstock which boils above 340°C and has a hydrogen content below 13.5 weight percent at hydrocracking inlet conditions, such that at least 30 weight percent of the feedstock is converted to hydrocarbon products which boil below the initial boiling point of the feedstock;

(b) hydrodewaxing the portion of the unconverted material of step (a) which has a kinematic viscosity of at least 3 cS at 100°C, a waxy VI of at least 125, a NOACK number of 20 or lower, a hydrogen content of at least 14 weight percent, a pour point of at least 10°C and a nitrogen content of no more than 30 ppm by uniformly distributing and contacting the material at an elevated temperature of up to 425°C (797°F) in the presence of cofed hydrogen at a pressure of at least 10,000 kPa (1450 psi) with a catalyst comprising a shape-selective, constrained intermediate pore molecular sieve wherein the molecular sieve possesses at least one channel with pores formed by rings which contain ten oxygen atoms which alternate with silicon or phosphorus atoms, the molecular sieve having an acidic functionality;

(c) hydrofinishing the effluent of step (b) under aromatics saturation conditions in contact with cofed

hydrogen and an effective aromatics saturation hydrofinishing catalyst having a metal hydrogenation function at a temperature of about 230°C (446°F) to about 343°C (650°F) and a pressure of at least 10,000 kPa (1450 psi) in order to obtain the dewaxed lubricant oil product.

(d) separating byproducts from the lubricant oil product via flashing and distillation of step (c).

2. The process of claim 1, wherein the unconverted material which is hydrodewaxed in step (b) boils at 315°C or above.

3. The process of claim 1, wherein step 1(a) further comprises the following steps:

(a) hydrotreating the hydrocarbon feed of step 1(a) in a hydrotreating zone over a catalyst having hydrodenitrogenation and hydrodesulfurization activity;

(b) passing the hydrotreated effluent of step 2(a) in cascade to a hydrocracking zone in which the feed is hydrocracked by contacting the feed with a hydrocracking catalyst comprising an amorphous material having large pores or a molecular sieve having large pores and further comprising a hydrogenation/dehydrogenation component, in the presence of hydrogen at elevated temperature and pressure to convert the hydrotreated effluent to lower boiling products at a hydrogen partial pressure from 3448 to 17,238 kPa (500 to 2500 psi), a temperature from 315°C to 455°C (600 to 850°F), a space velocity from 0.5 to 10 LHSV and a hydrogen:oil ratio of from 1000 to 5000SCF/BBl, a conversion of at least 30 wt% per pass to form a hydrocracked effluent from which at least 90% of the nitrogen has been removed;

(c) passing the hydrocracked effluent of step (b) to a separation zone for the removal of products, the unconverted portion being passed to a vacuum distillation zone which is operated at a tower bottom temperature ranging from about 300 to about 380°C under tower bottom

pressures ranging from about 20 to about 300 mmHg, thereby producing product fractions and a bottom fraction

(d) passing the product from step 3(c) to the dewaxing zone of step 1(b).

4. The process of step 3(c), wherein at least a portion of the bottom fraction is recycled to the hydrocracking zone of step 2(b).

5. The process of claim 1 or 2, wherein the shape-selective, intermediate pore molecular sieve material of step 1(b) is selected from the group consisting of ZSM-5, ZSM-23, ZSM-35, ZSM-11, SAPO-11 or combinations thereof, wherein each of these catalysts is loaded with a noble metal.

6. The process of claim 1 or 2, wherein the shape-selective, intermediate pore molecular sieve of step 1(b) is HZSM-5.

7. The process of claim 5, wherein the shape selective, intermediate pore molecular sieve material possesses a Constraint Index of from 0.5 to 12 and an alpha of less than 300.

8. The process of claim 7, wherein the alpha value is less than 30.

9. The process of claim 8, wherein the alpha value is less than 10.

10. The process of claim 5, wherein the molecular sieve material is loaded with from 0.2 to 1.2 wt% noble metal.

11. The process of claim 1 or 2, wherein the hydrofinishing catalyst of step 1(c) comprises at least one

Group VIIIA and at least one Group VIA metal (IUPAC) on a porous solid support.

12. The process of claim 1 wherein the hydrofinishing catalyst of step 1(c) comprises nickel and tungsten metals on a fluorided porous alumina support which comprises alumina or a mixture of silica and alumina.

13. The process of claim 1 wherein the dewaxing zone and hydrofinishing zone are operated at substantially the same pressure, and wherein the entire dewaxed oil stream from the dewaxing stage is passed directly to the hydrofinishing zone.

14. The process of claim 10 wherein dewaxing catalyst ages at a rate not greater than about 0.1°C/day at a pressure greater than 10,000 kPa.

15. The process of claim 1, wherein the hydrodewaxing of step 1(b) occurs in at least two dewaxing zones.

16. The process of claim 1, wherein the hydrofinishing of step 1(c) occurs in at least two dewaxing zones.

17. The process of claim 1, wherein the dewaxed lubricant oil product boils above about 370°C, possesses a KV in the range of 4 to 10 cSt at 100°C, and a UV absorptivity at 315 nm of less than 0.001.L/g-cm.

18. The process of claim 17, wherein the dewaxed lubricant oil product possesses a UV absorptivity at 315 nm of less than 0.001 L/g-cm.

19. The process of claim 1 or 2, wherein the heavy hydrocarbon feedstock comprises vacuum gas oils, deasphalted raffinates, or a mixture of both.

20. The process of claim 1 or 2, wherein the hydrodewaxing zone of step 1(b) comprises a series of vertically arranged fixed bed catalytic reactors, wherein quench streams of H_2 gas are located in between the beds for use in temperature reduction.

21. The process of claim 1 or 2, wherein the hydrofinishing zone of step 1(c) comprises a series of vertically arranged fixed bed catalytic reactors, wherein quench streams of H_2 gas are located in between the beds for use in temperature reduction.

22. The process of claim 1, wherein the NOACK number is no greater than 10.

23. The process of claim 22, wherein the NOACK number is no greater than 5.

24. The process of claim 2(c), wherein the bottoms of the vacuum distillation zone have a NOACK number of no more than 20.

25. The process of claim 24, wherein the bottoms of the vacuum distillation zone have a NOACK number of no greater than 10.

26. The process of claim 25, wherein the bottoms of the vacuum distillation zone have a NOACK number of no greater than 5.

27. The process of claim 1, wherein the aromatics content of the dewaxed lubricant and product is no greater than 2 wt %.

28. The process of claim 1, wherein the dewaxed oil lubricant product exhibits color stability after exposure to sunlight and ambient air for 10 days.

29. The process of claim 1, wherein the dewaxed lubricant oil product has a 10% distillation point of 357°C or higher.

30. The process of claim 29, wherein the dewaxed lubricant oil product has a 10% distillation point of 413°C or higher.

31. The process of claim 30, wherein the dewaxed lubricant oil product has a distillation point of 432°C or higher.

32. The process of claim 1, wherein the dewaxed lubricant oil product has a pour point in the range from -50°C to -4°C.

33. The process of claim 1 wherein the dewaxed lubricant oil product has a hydrogen content of at least 14.3 wt.% and a VI of 120 or greater.

FIG. 1

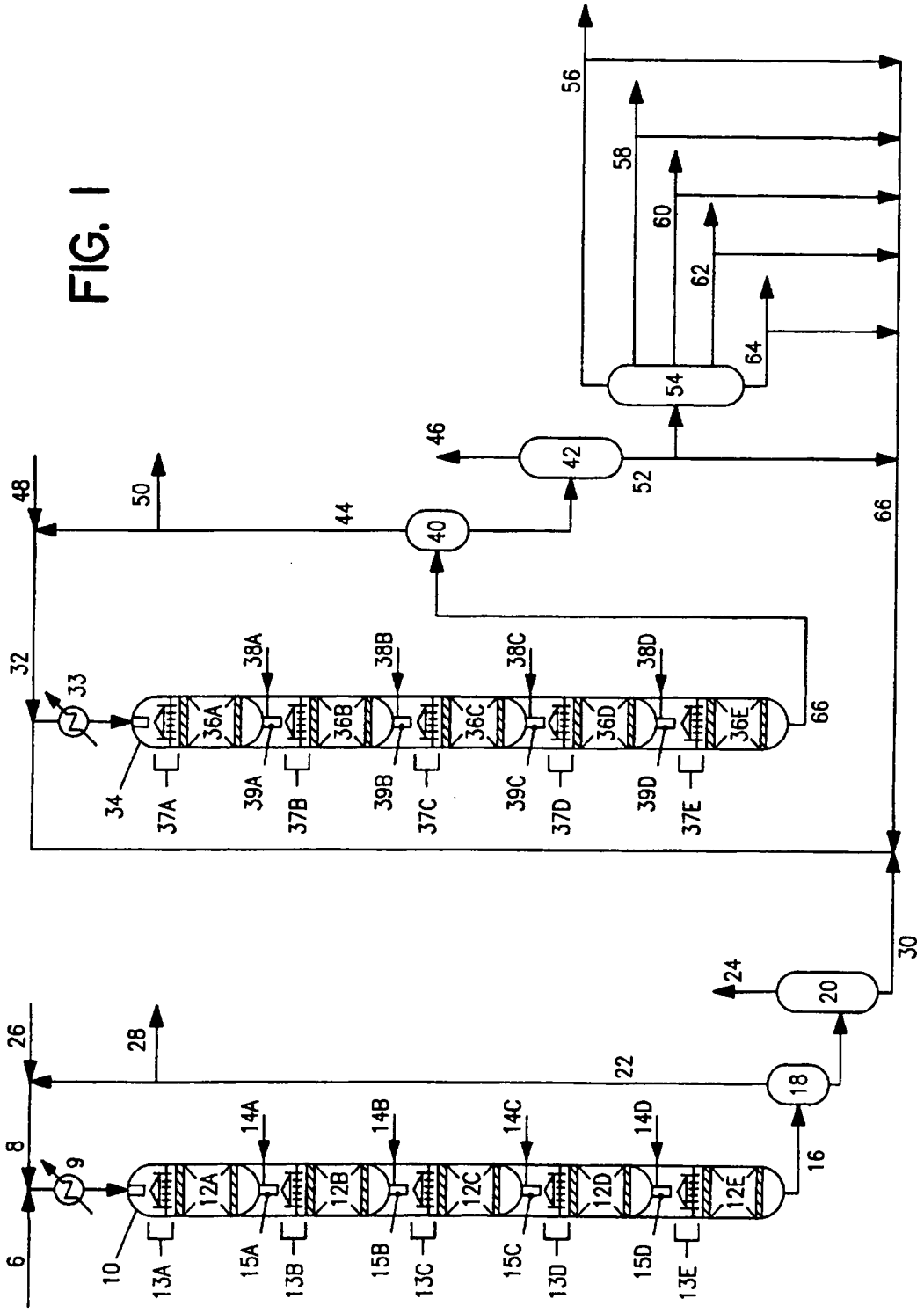
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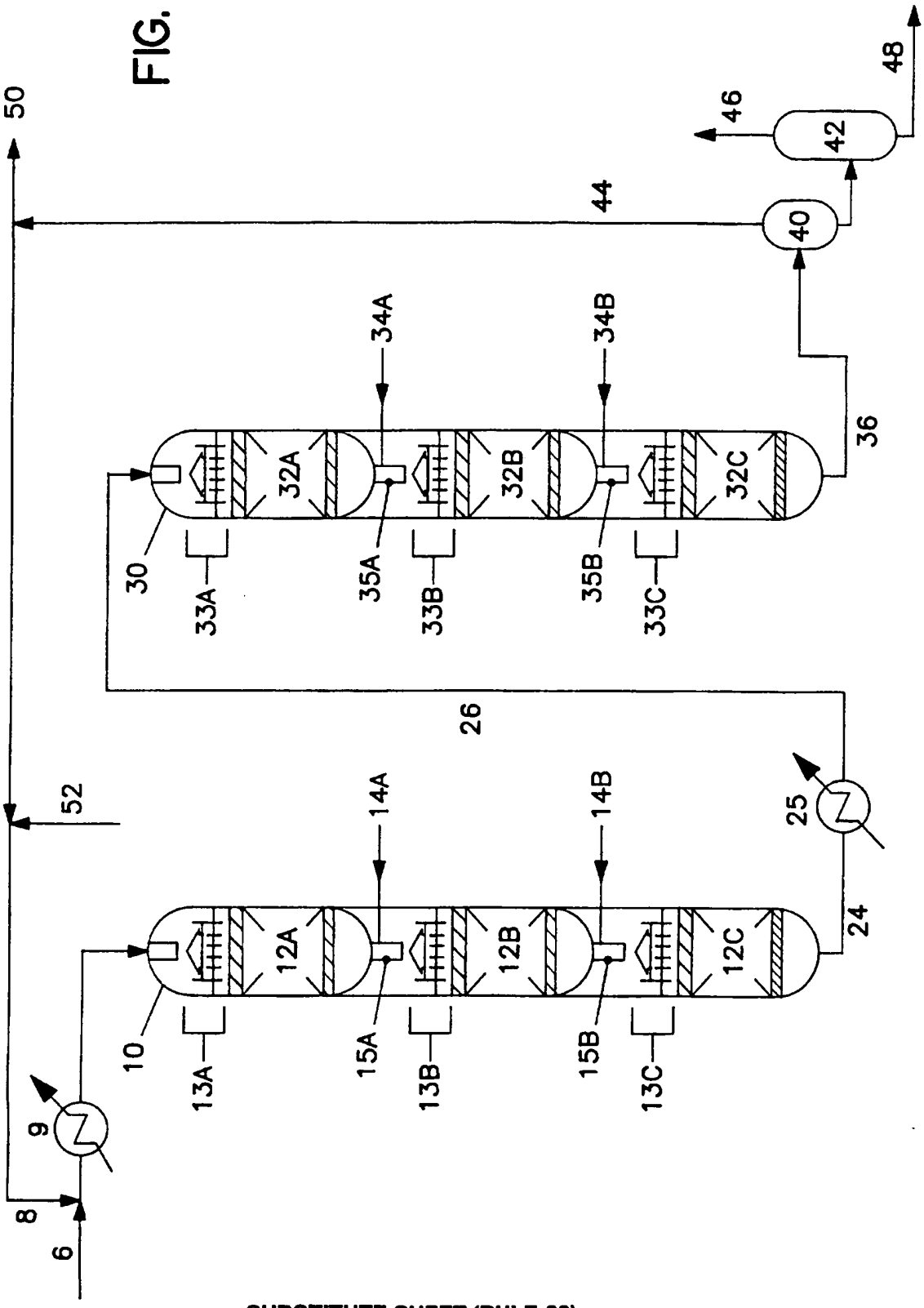
FIG. 2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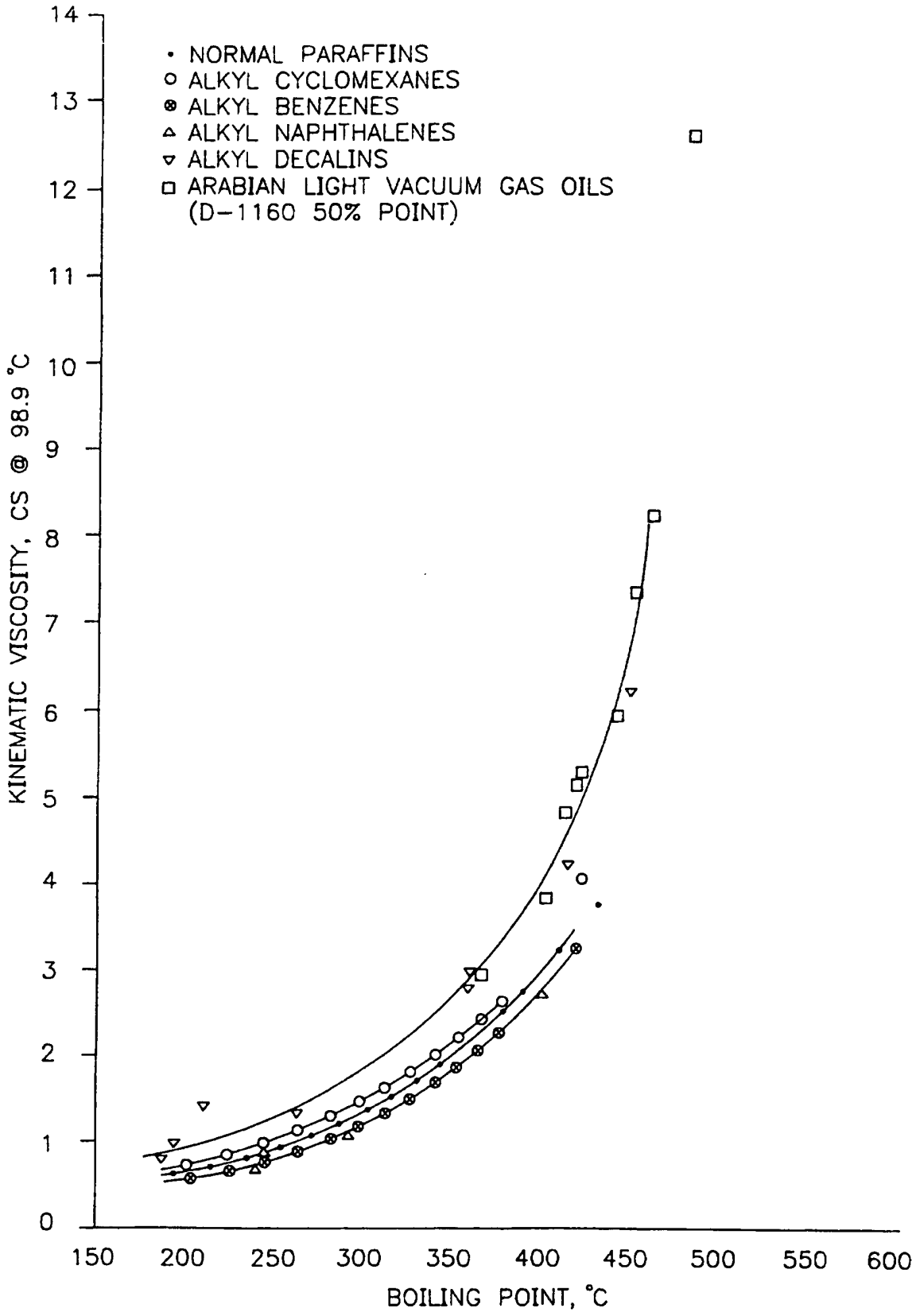
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ALKYL NAPHTHALENES
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(D-1160 50% POINT)
KINEMATIC VISCOSITY, CS @ 98.9 °C
BOILING POINT, °C
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3
4
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FIG. 3

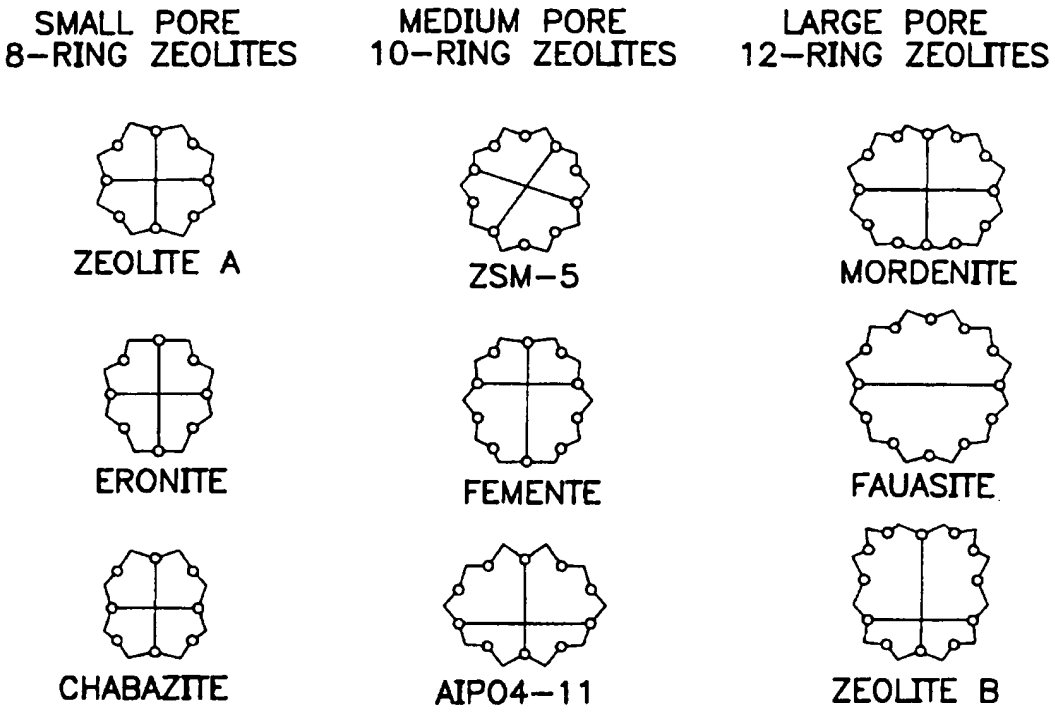
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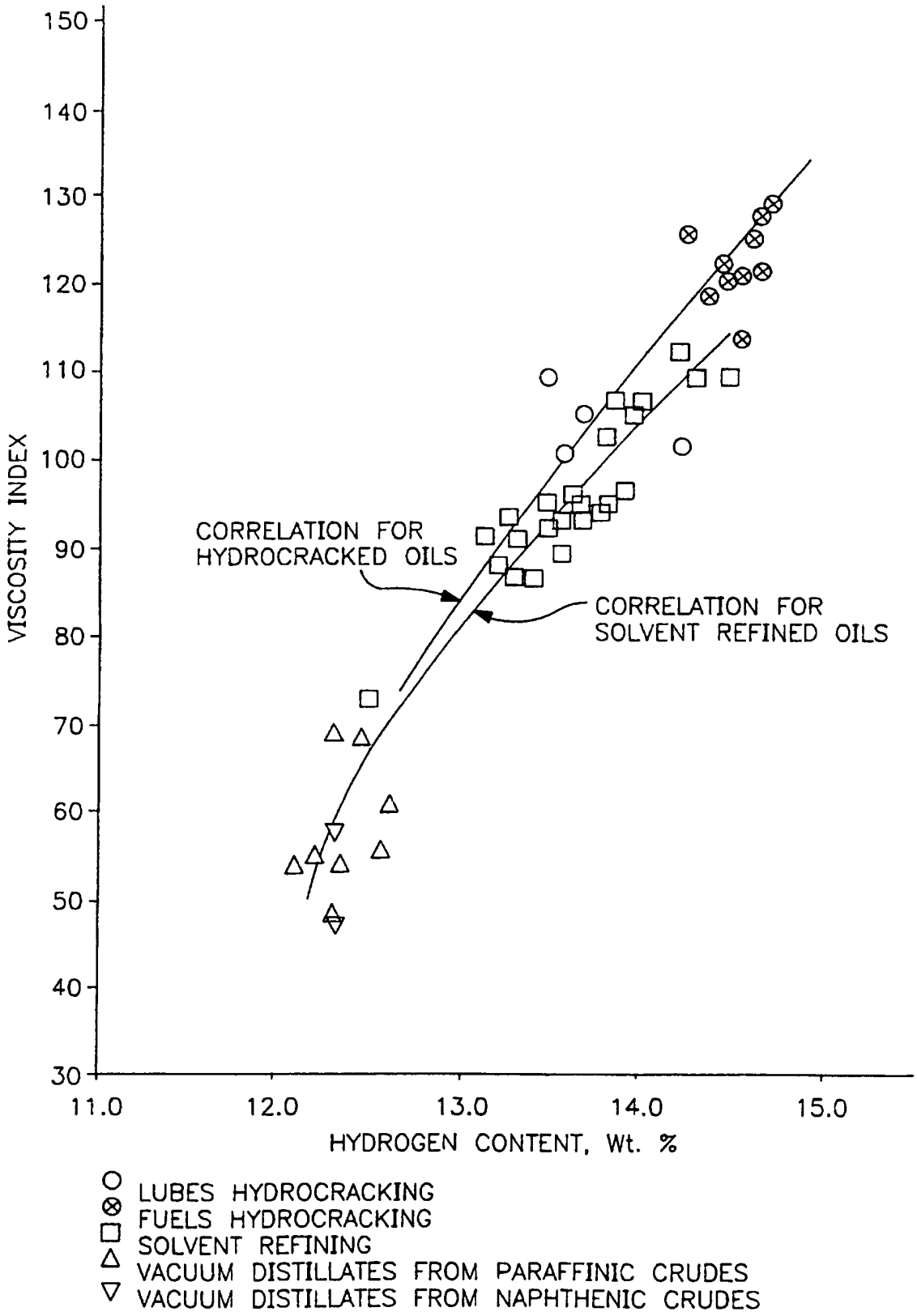
FIG. 4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13.0
14.0
15.0
HYDROGEN CONTENT, Wt. %
CORRELATION FOR HYDROCRACKED OILS
CORRELATION FOR SOLVENT REFINED OILS
LUBES HYDROCRACKING
FUELS HYDROCRACKING
SOLVENT REFINING
VACUUM DISTILLATES FROM PARAFFINIC CRUDES
VACUUM DISTILLATES FROM NAPHTHENIC CRUDES

FIG. 5

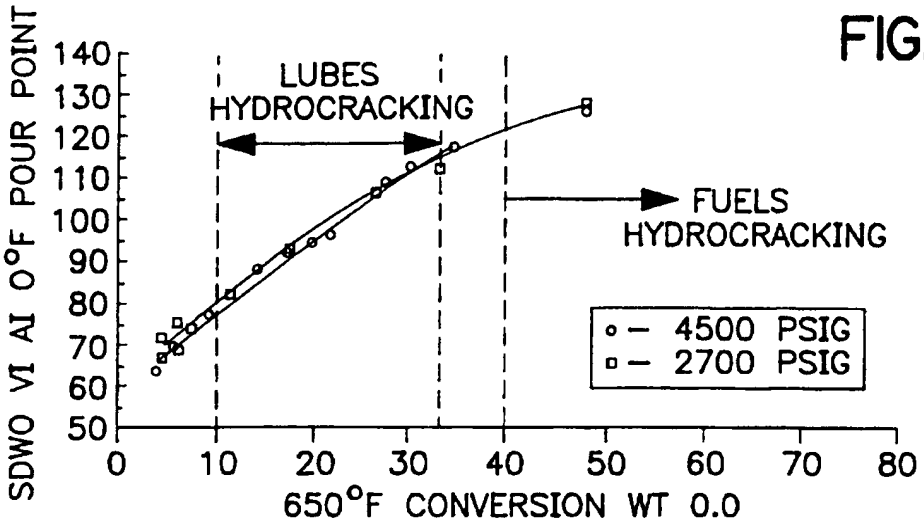


FIG. 6A

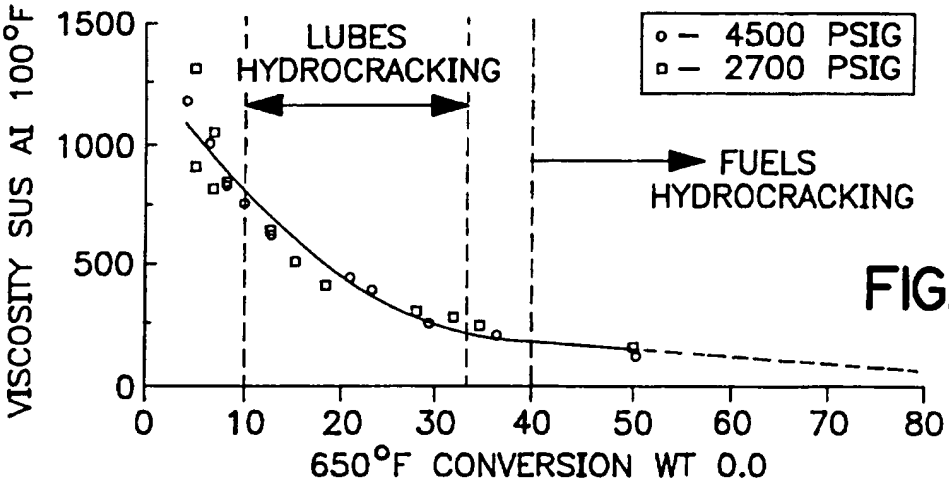


FIG. 6B

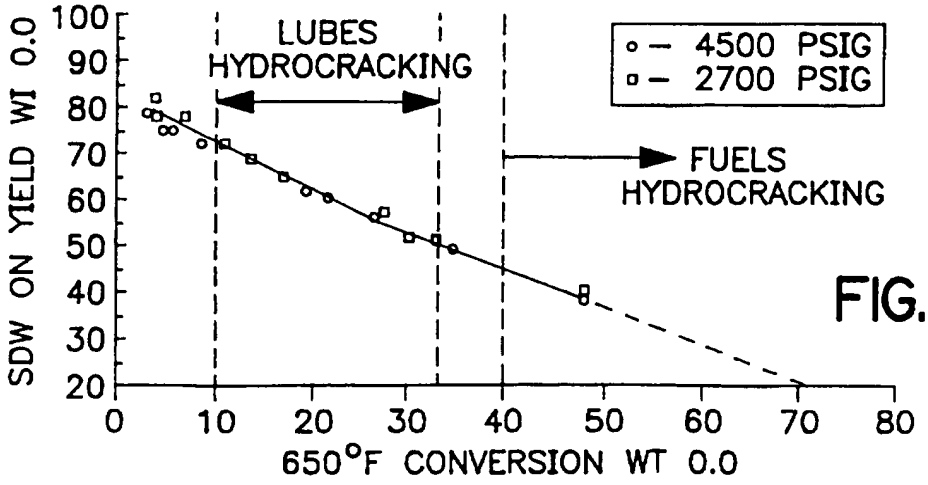


FIG. 6C

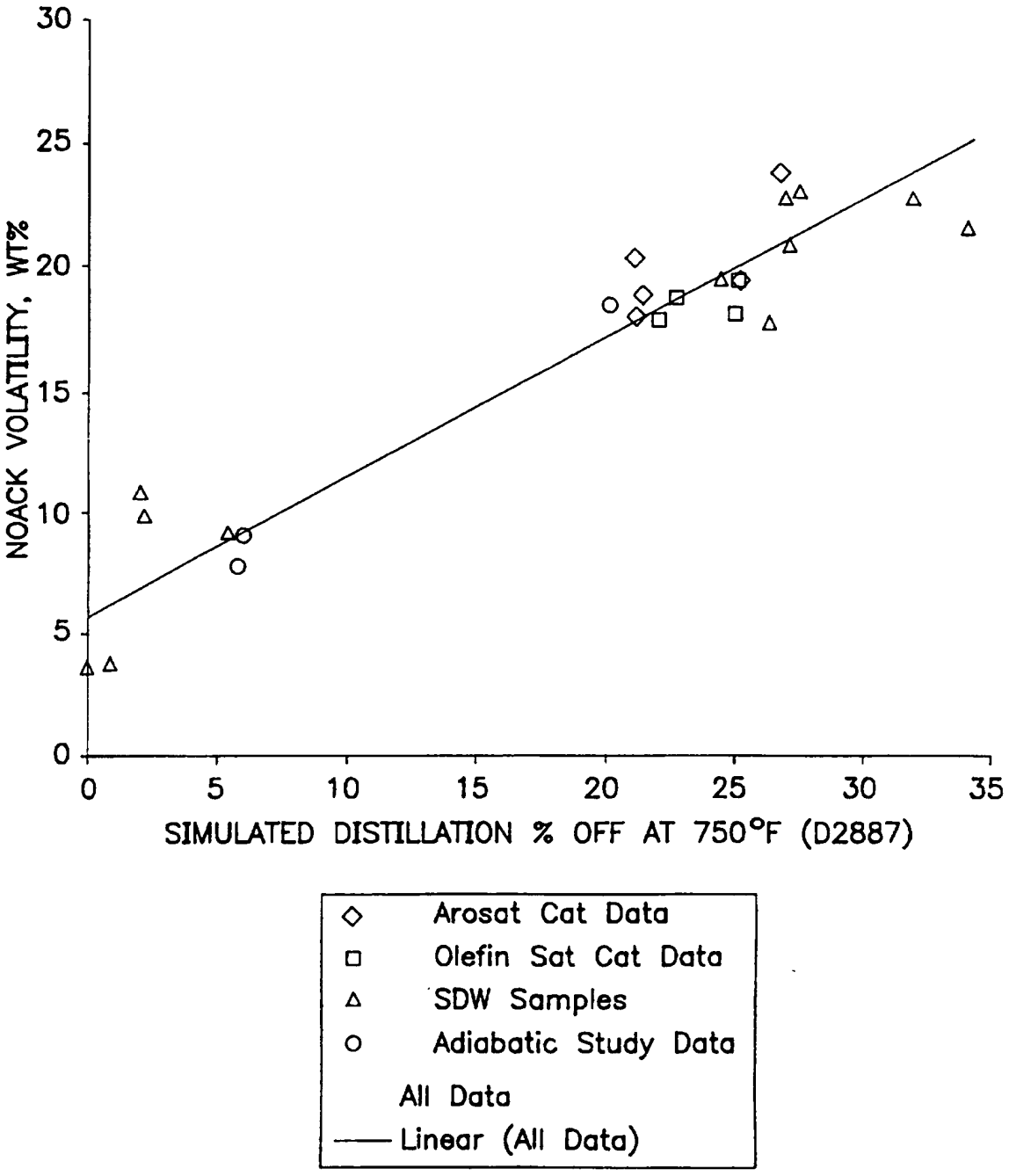

NOACK VOLATILITY, WT%
SIMULATED DISTILLATION % OFF AT 750°F (D2887)
0
5
10
15
20
25
30
35
Arosat Cat Data
Olefin Sat Cat Data
SDW Samples
Adiabatic Study Data
All Data
Linear (All Data)

FIG. 7

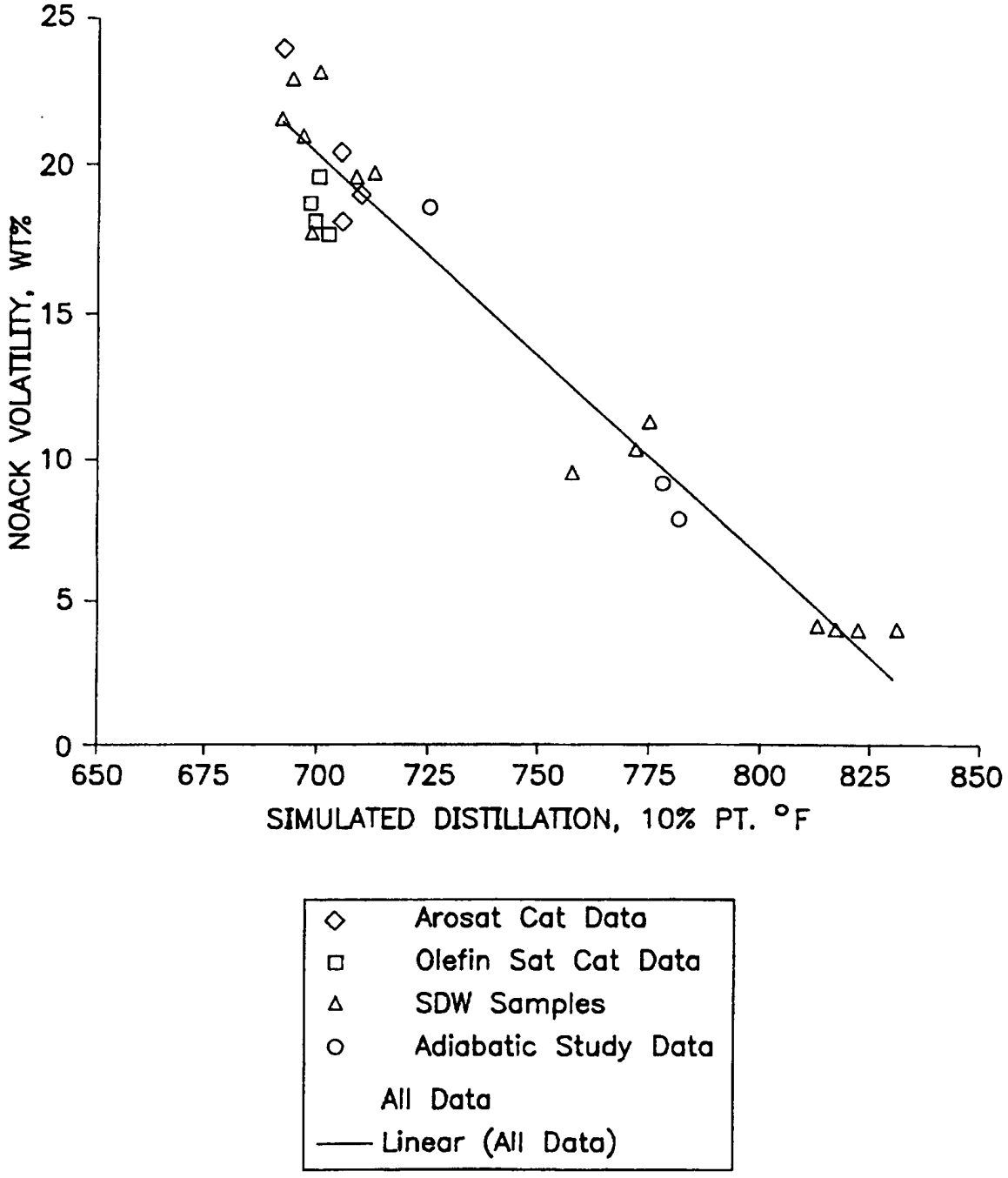

25
20
15
10
5
0
NOACK VOLATILITY, WT%
650
675
700
725
750
775
800
825
850
SIMULATED DISTILLATION, 10% PT. °F
Arosat Cat Data
Olefin Sat Cat Data
SDW Samples
Adiabatic Study Data
All Data
Linear (All Data)

FIG. 8

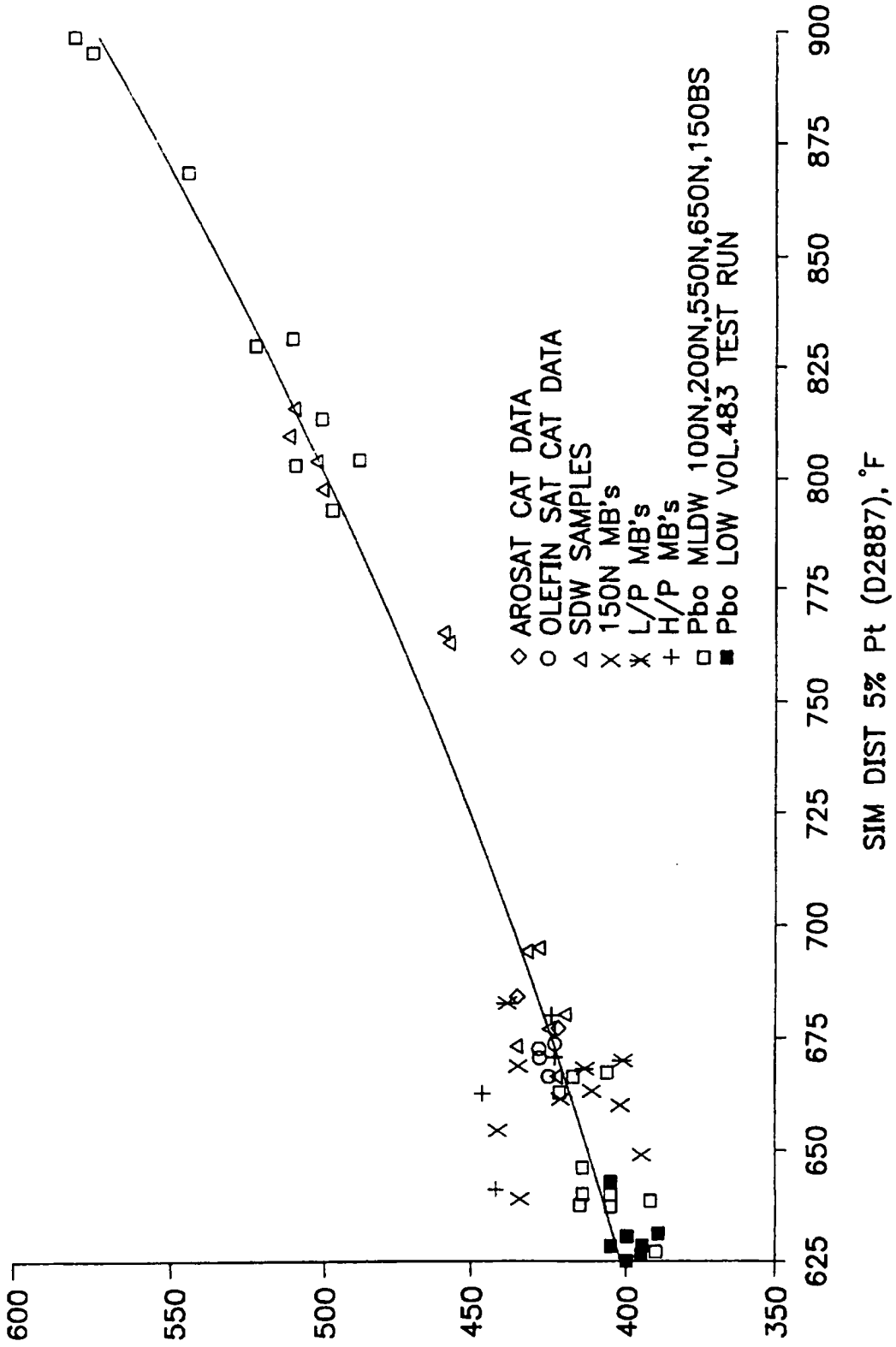
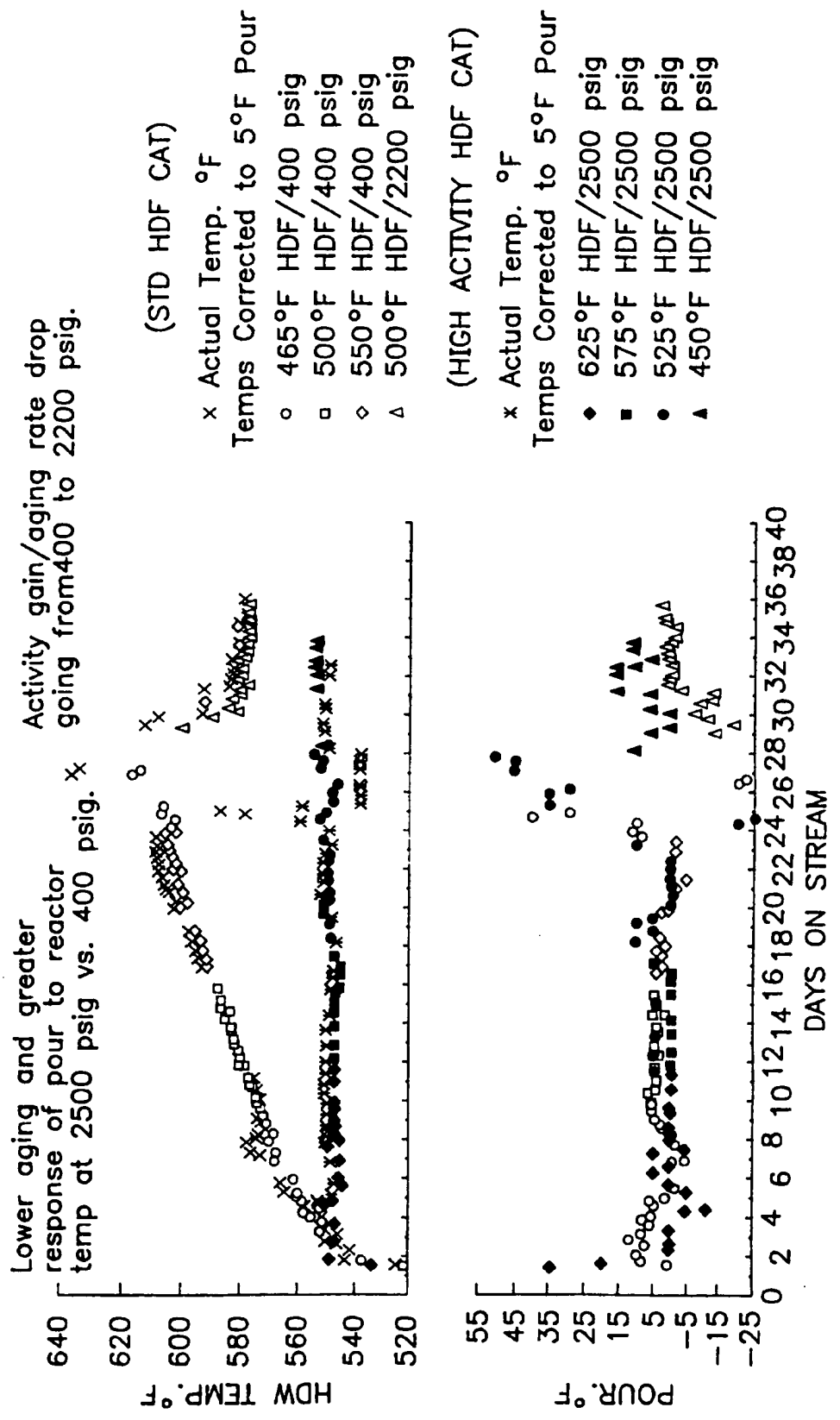
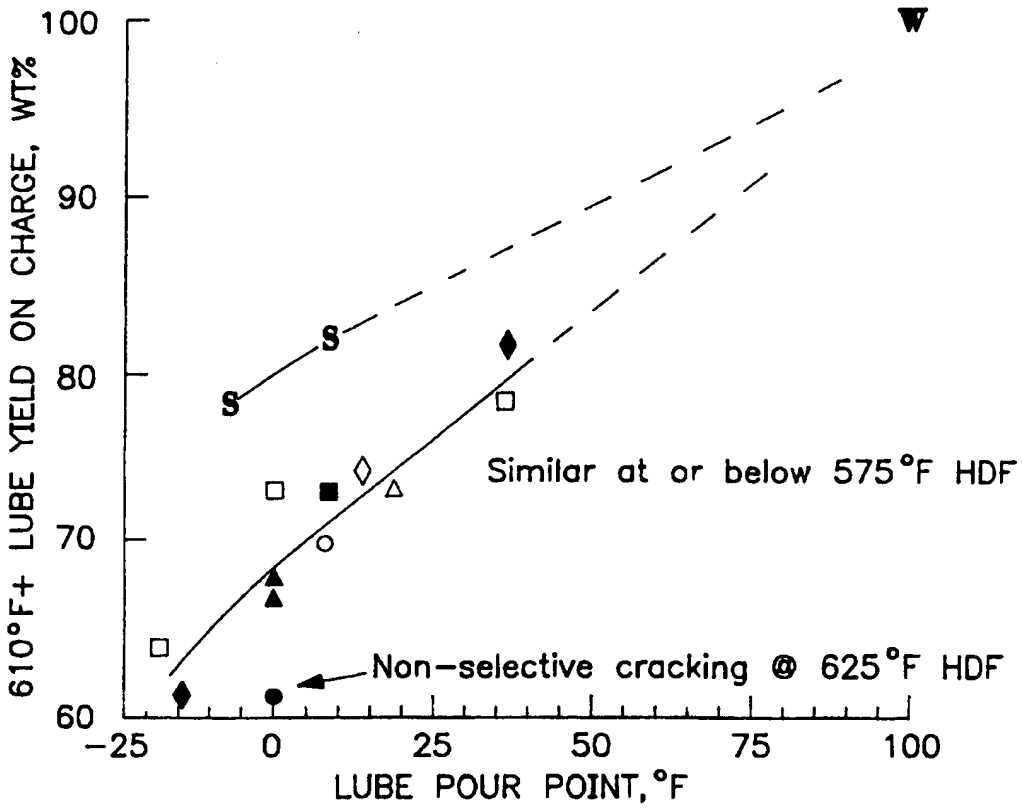

COC FLASH POINT, °F
600
550
500
450
400
350
625
650
675
700
725
750
775
800
825
850
875
900
SIM DIST 5% Pt (D2887), °F
◇ AROSAT CAT DATA
○ OLEFIN SAT CAT DATA
△ SDW SAMPLES
× 150N MB's
✳ L/P MB's
+ H/P MB's
□ Pbo MLDW 100N,200N,550N,650N,150BS
■ Pbo LOW VOL.483 TEST RUN

FIG. 9

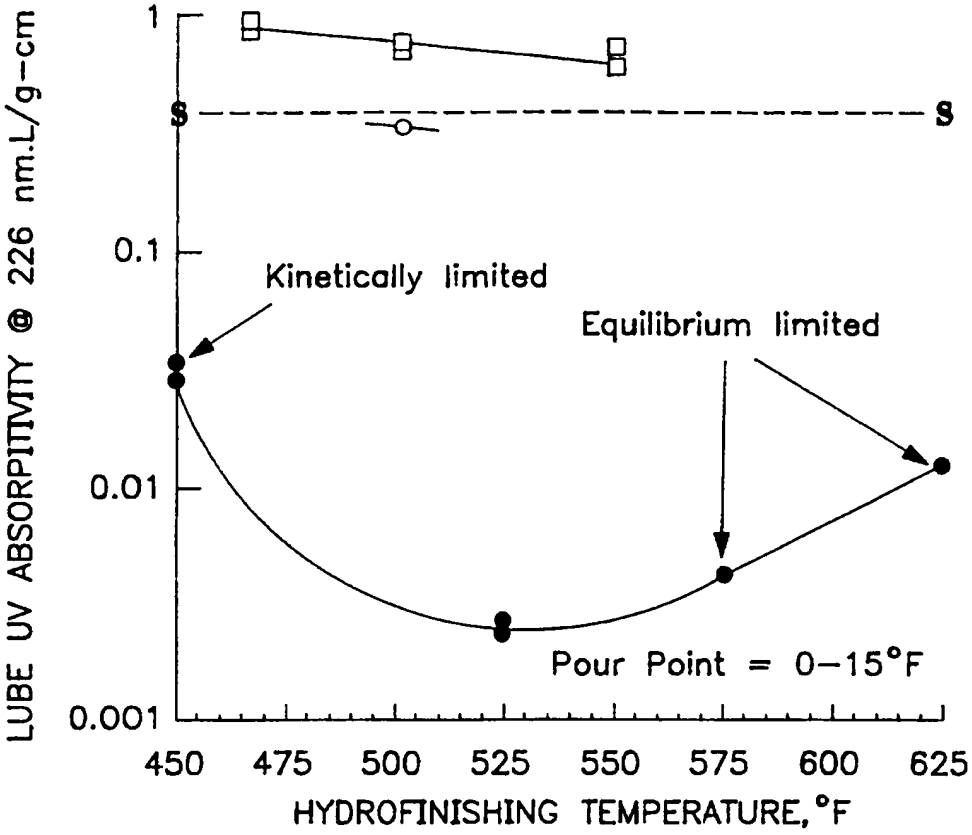
FIG. 10


Lower aging and greater response of pour to reactor temp at 2500 psig vs. 400 psig.
Activity gain/aging rate drop going from400 to 2200 psig.
(STD HDF CAT)
x Actual Temp. °F
Temps Corrected to 5°F Pour
o 465°F HDF/400 psig
□ 500°F HDF/400 psig
◇ 550°F HDF/400 psig
△ 500°F HDF/2200 psig
(HIGH ACTIVITY HDF CAT)
x Actual Temp. °F
Temps Corrected to 5°F Pour
◆ 625°F HDF/2500 psig
■ 575°F HDF/2500 psig
● 525°F HDF/2500 psig
▲ 450°F HDF/2500 psig
HDW TEMP. °F
640
620
600
580
560
540
520
POUR. °F
55
45
35
25
15
5
-5
-15
-25
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40
DAYS ON STREAM



W	WAXY CHARGE
S	SOLVENT DEWAXING (dry wax basis)
	MLDW: Std HDF Cat @ 400 psig
□	465 °F HDF
◊	500 °F HDF
△	550 °F HDF
	MLDW: Std HDF Cat @ 2200 psig
○	500 °F HDF
	MLDW: Arosat HDF Cat @ 2500 psig
■	450 °F HDF
♦	525 °F HDF
▲	575 °F HDF
●	625 °F HDF

FIG. 11


LUBE UV ABSORPTIVITY @ 226 nm.L/g-cm
1
0.1
0.01
0.001
S
S
Kinetically limited
Equilibrium limited
Pour Point = 0–15°F
450
475
500
525
550
575
600
625
HYDROFINISHING TEMPERATURE, °F

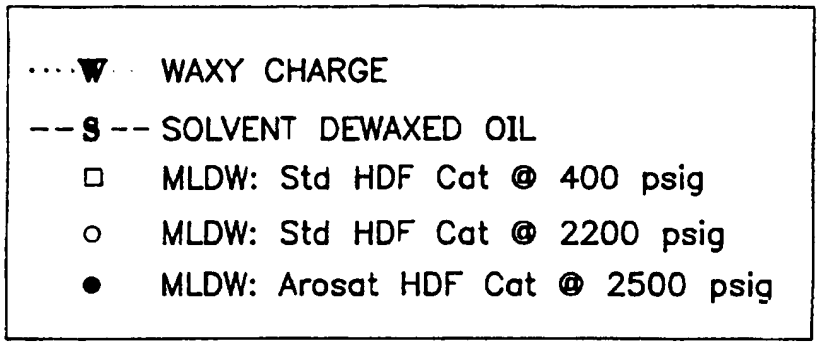

W WAXY CHARGE
S SOLVENT DEWAXED OIL
MLDW: Std HDF Cat @ 400 psig
MLDW: Std HDF Cat @ 2200 psig
MLDW: Arosat HDF Cat @ 2500 psig

FIG. 12

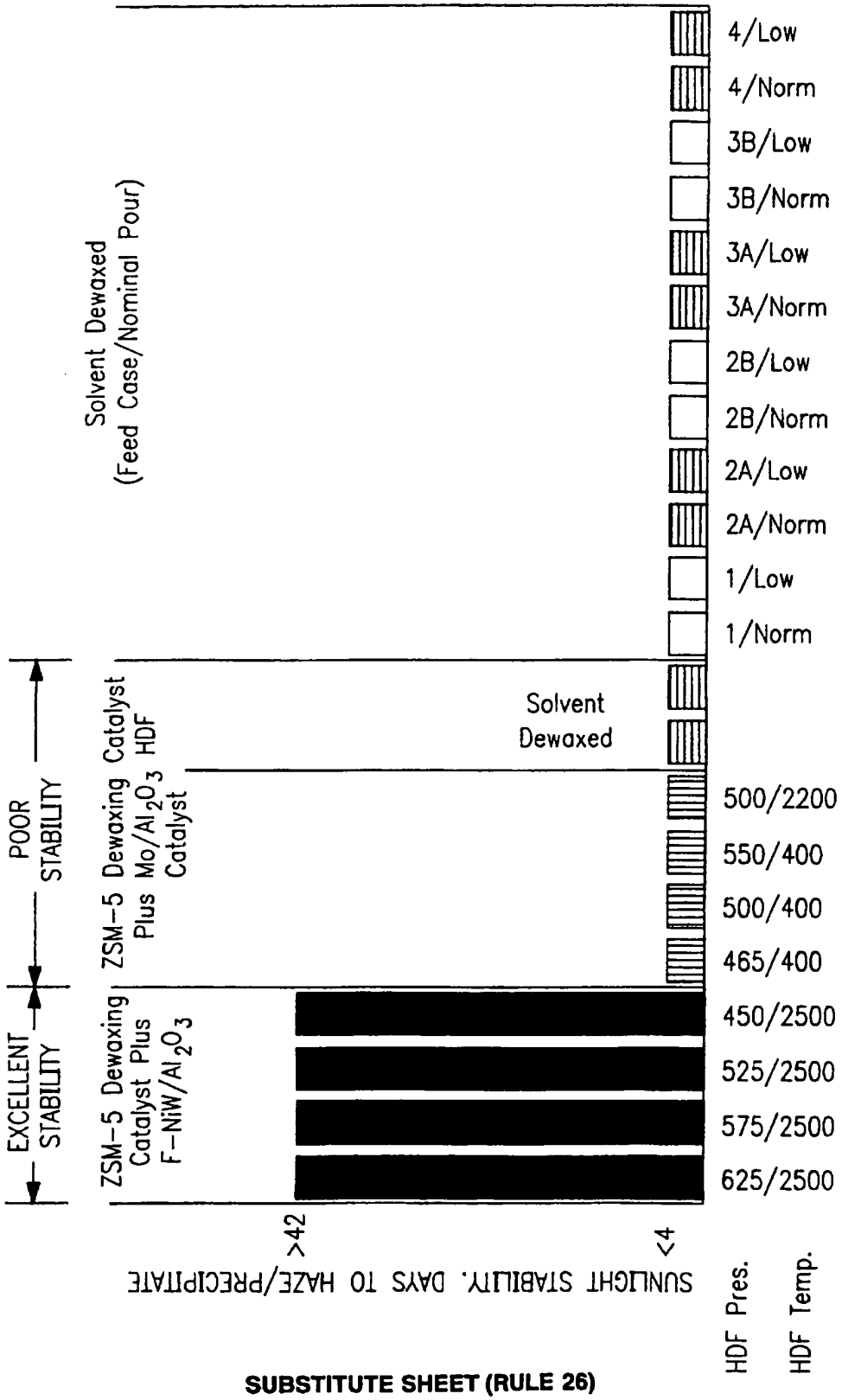

SUNLIGHT STABILITY, DAYS TO HAZE/PRECIPITATE
>42
<4
HDF Pres.
HDF Temp.
EXCELLENT STABILITY
POOR STABILITY
ZSM-5 Dewaxing Catalyst Plus F-NiW/Al2O3
ZSM-5 Dewaxing Catalyst Plus Mo/Al2O3 Catalyst HDF
Solvent Dewaxed
Solvent Dewaxed (Feed Case/Nominal Pour)
625/2500
575/2500
525/2500
450/2500
465/400
500/400
550/400
500/2200
1/Norm
1/Low
2A/Norm
2A/Low
2B/Norm
2B/Low
3A/Norm
3A/Low
3B/Norm
3B/Low
4/Norm
4/Low

FIG. 13

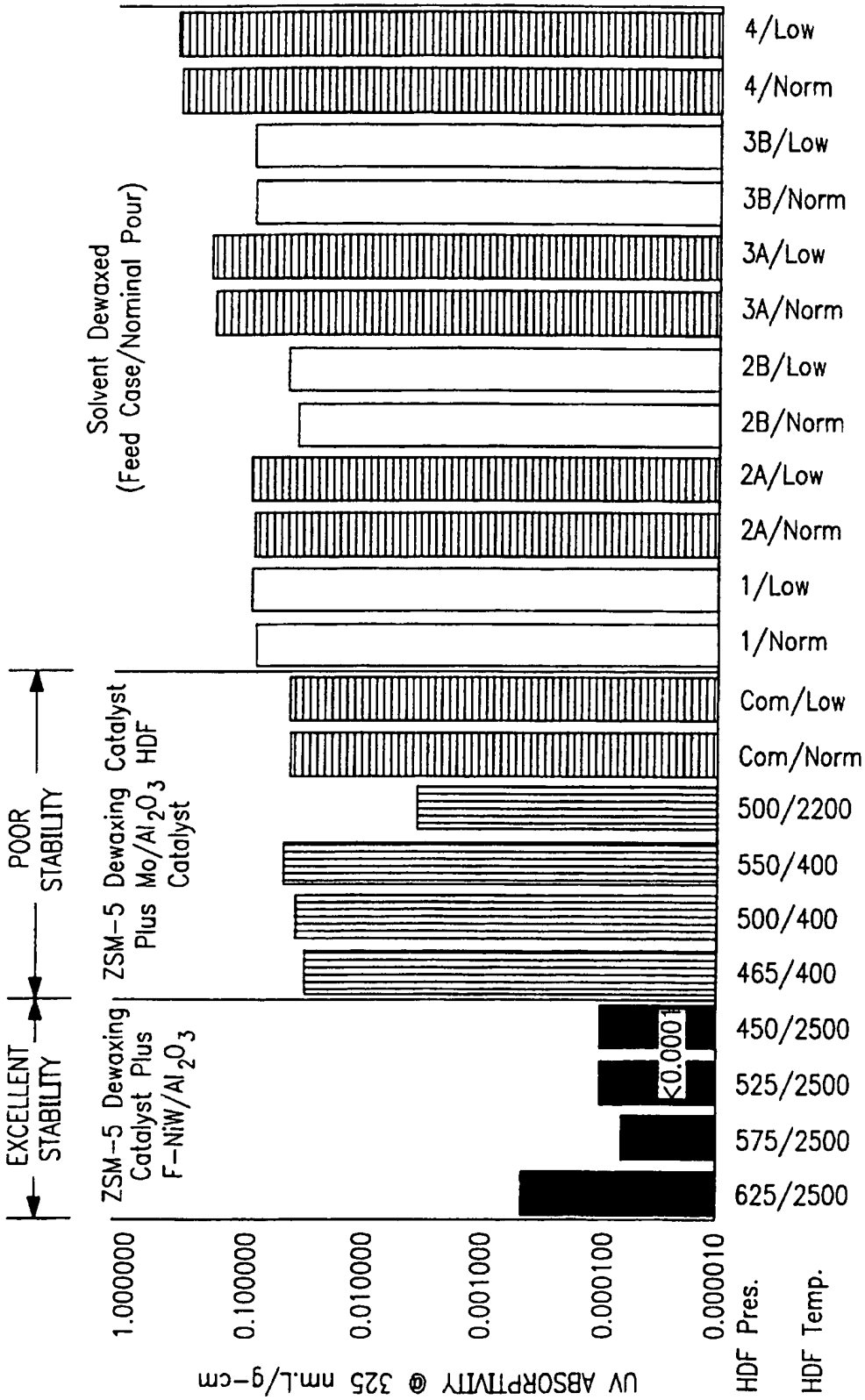

UV ABSORPTIVITY @ 325 nm.L/g-cm
1.000000
0.100000
0.010000
0.001000
0.000100
0.000010
HDF Pres.
HDF Temp.
EXCELLENT STABILITY
POOR STABILITY
ZSM-5 Dewaxing Catalyst Plus F-NiW/Al2O3
ZSM-5 Dewaxing Catalyst Plus Mo/Al2O3 HDF Catalyst
Solvent Dewaxed (Feed Case/Nominal Pour)
<0.0001
625/2500
575/2500
525/2500
450/2500
465/400
500/400
550/400
500/2200
Com/Norm
Com/Low
1/Norm
1/Low
2A/Norm
2A/Low
2B/Norm
2B/Low
3A/Norm
3A/Low
3B/Norm
3B/Low
4/Norm
4/Low

FIG. 14

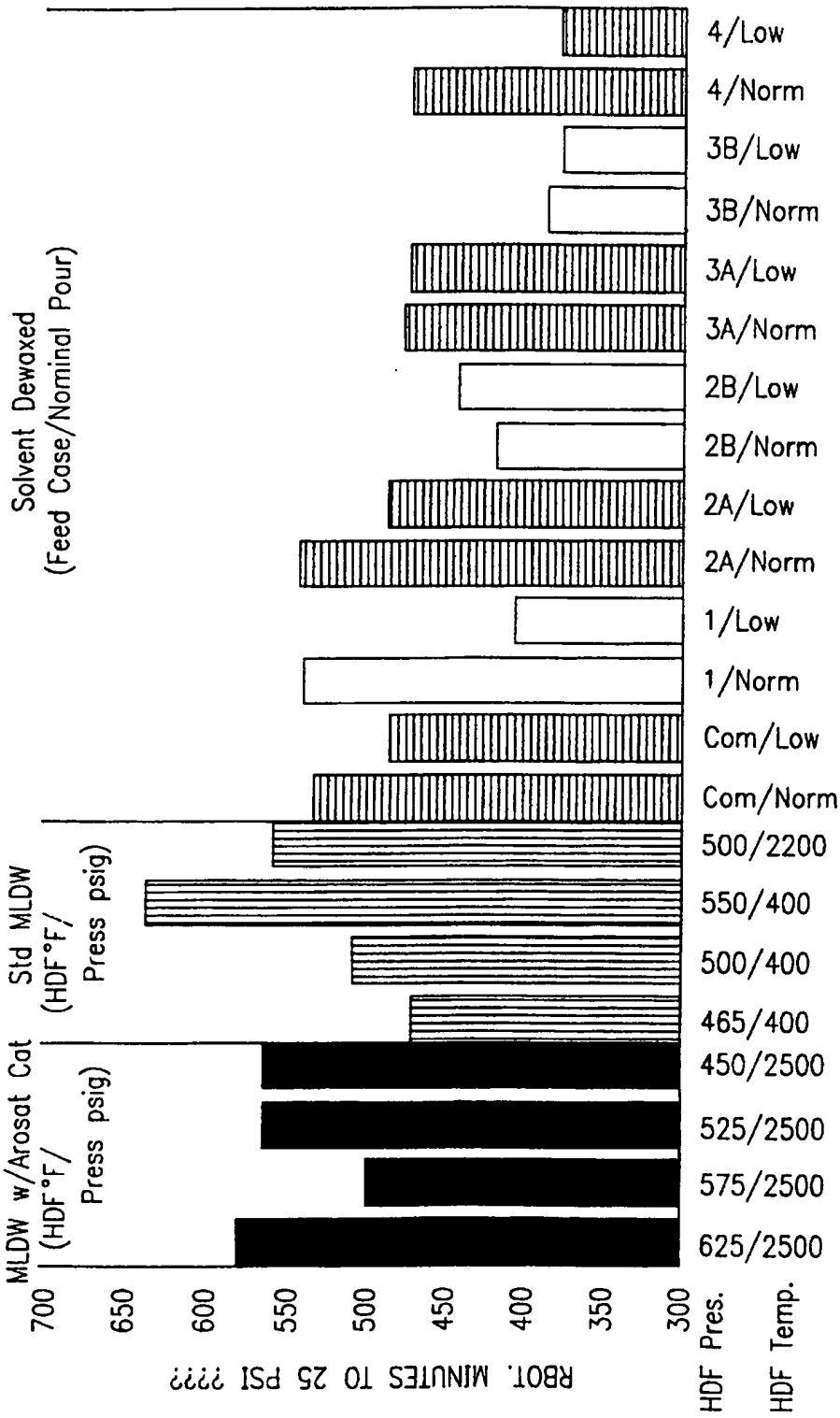

Solvent Dewaxed
(Feed Case/Nominal Pour)
4/Low
4/Norm
3B/Low
3B/Norm
3A/Low
3A/Norm
2B/Low
2B/Norm
2A/Low
2A/Norm
1/Low
1/Norm
Com/Low
Com/Norm
Std MLDW
(HDF°F/
Press psig)
500/2200
550/400
500/400
465/400
MLDW w/Arosat Cat
(HDF°F/
Press psig)
450/2500
525/2500
575/2500
625/2500
700
650
600
550
500
450
400
350
300
HDF Pres.
HDF Temp.
RBOT, MINUTES TO 25 PSI ????

FIG. 15

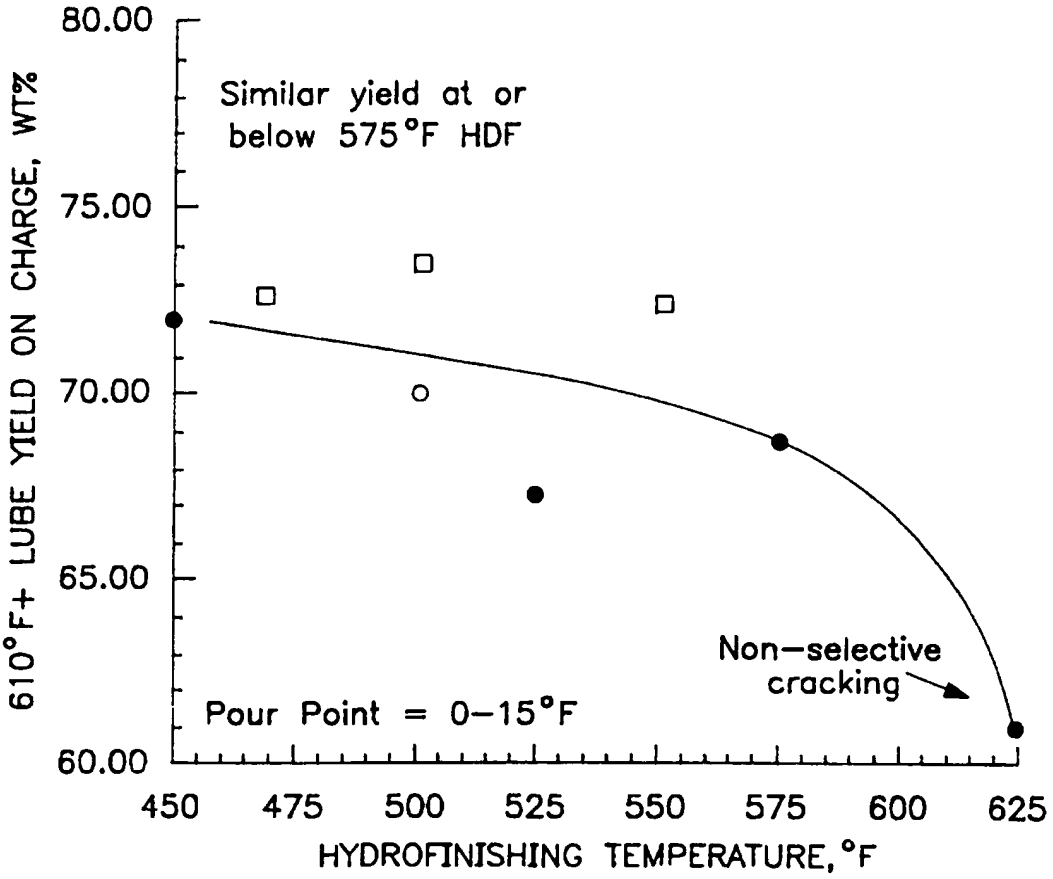

80.00
75.00
70.00
65.00
60.00
610°F+ LUBE YIELD ON CHARGE, WT%
Similar yield at or below 575°F HDF
Non-selective cracking
Pour Point = 0-15°F
450
475
500
525
550
575
600
625
HYDROFINISHING TEMPERATURE, °F
MLDW: Std HDF Cat @ 400 psig
MLDW: Std HDF Cat @ 2200 psig
MLDW: Arosat HDF Cat @ 2500 psig

FIG. 16

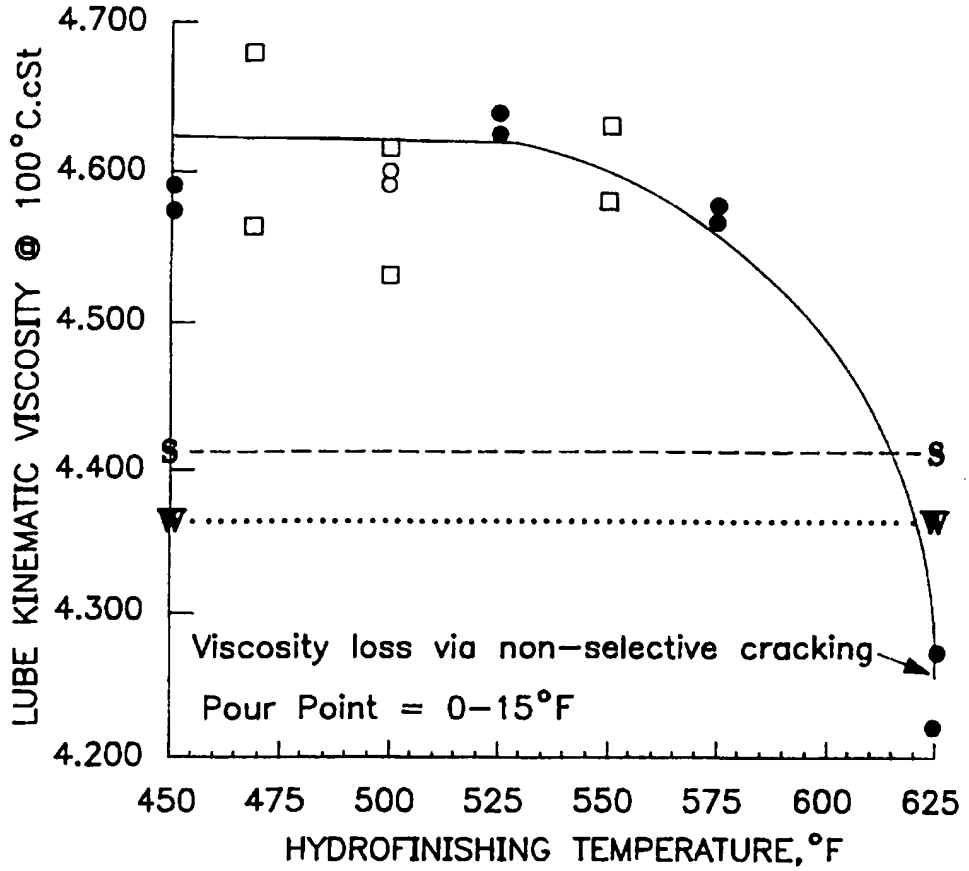
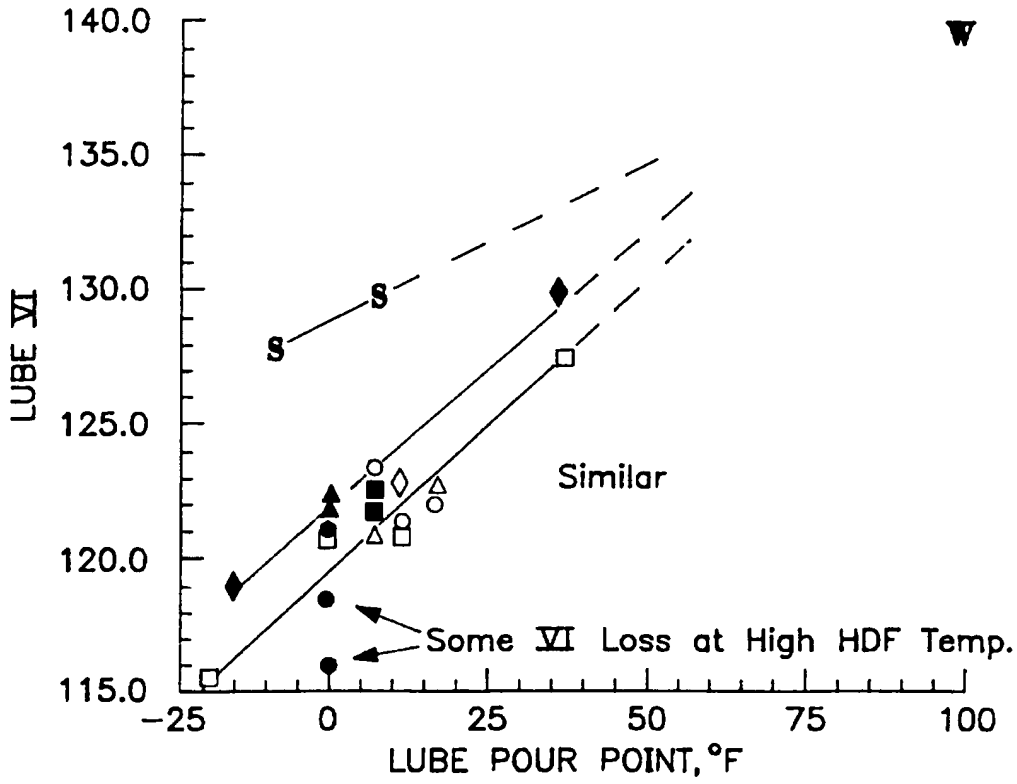
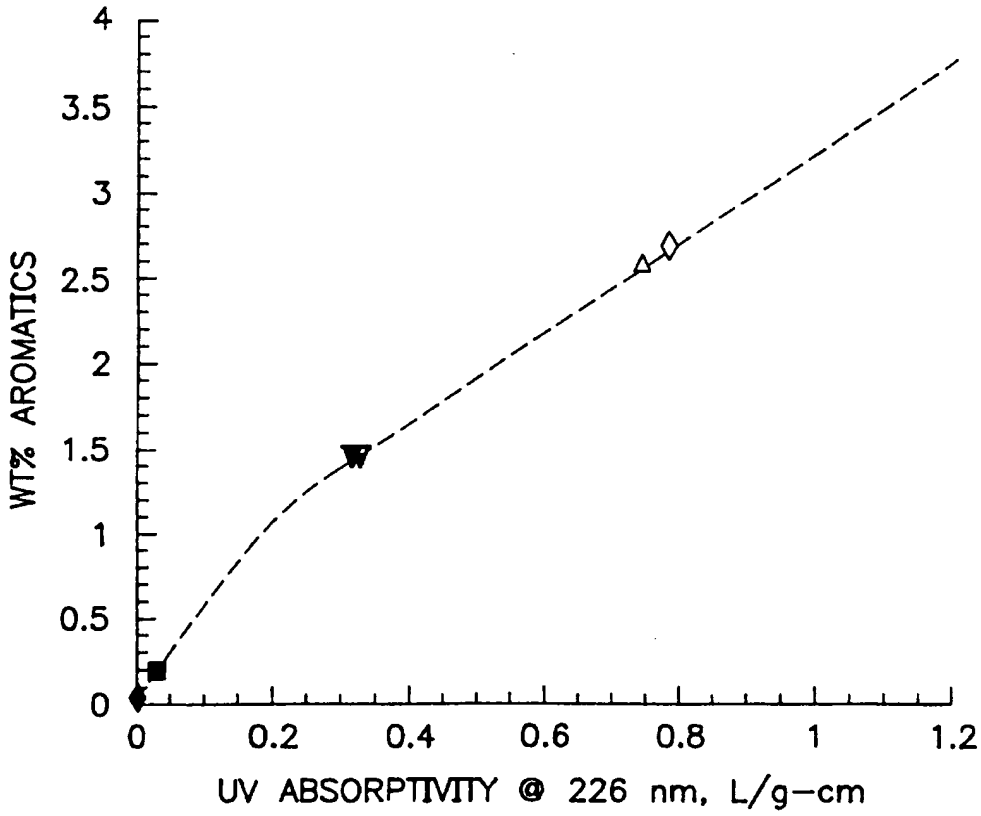

4.700
4.600
4.500
4.400
4.300
4.200
LUBE KINEMATIC VISCOSITY @ 100°C.cSt
S
S
W
Viscosity loss via non-selective cracking
Pour Point = 0-15°F
450
475
500
525
550
575
600
625
HYDROFINISHING TEMPERATURE, °F
W WAXY CHARGE
S SOLVENT DEWAXED OIL
MLDW: Std HDF Cat @ 400 psig
MLDW: Std HDF Cat @ 2200 psig
MLDW: Arosat HDF Cat @ 2500 psig

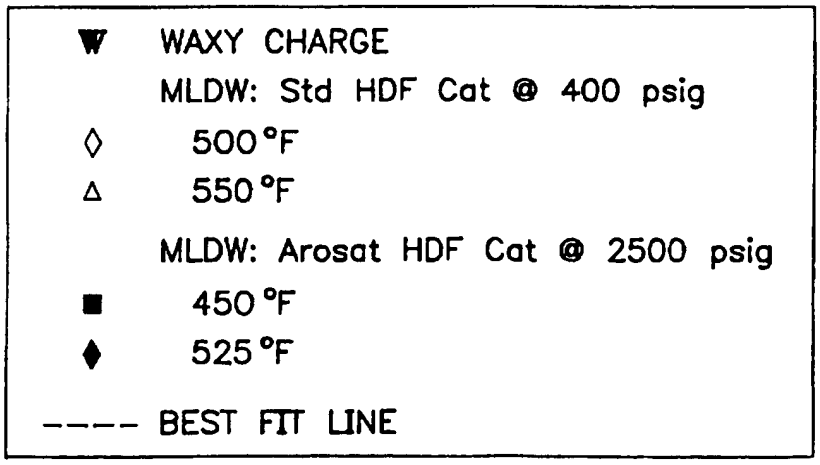
FIG. 17



W	WAXY CHARGE
S	SOLVENT DEWAXED OIL
	MLDW: Std HDF Cat @ 400 psig
□	465 °F HDF
◊	500 °F HDF
△	550 °F HDF
	MLDW: Std HDF Cat @ 2200 psig
○	500 ° HDF
	MLDW: Arosat HDF Cat @ 2500 psig
■	450 °F HDF
♦	525 °F HDF
▲	575 °F HDF
●	625 °F HDF

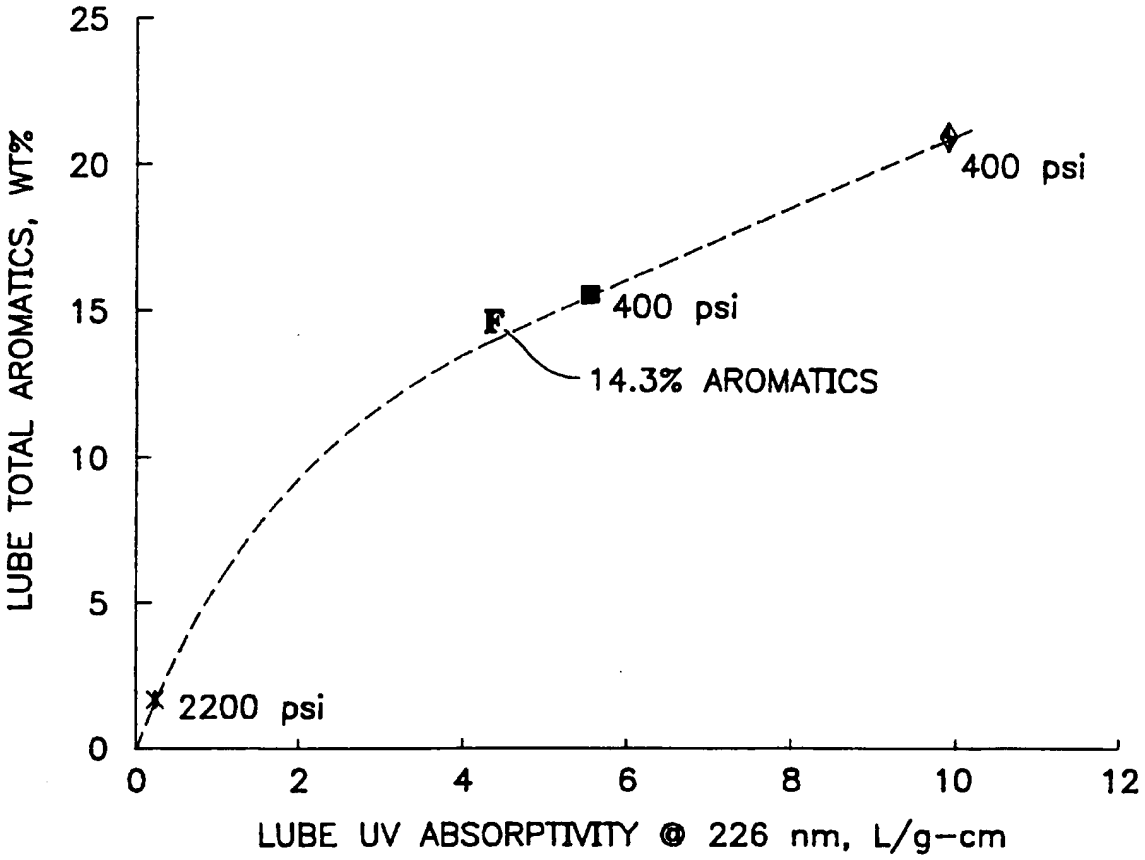
FIG. 18





Total aromatics determined using
HPLC seperation with high sensitivity
light scattering mass detector

FIG. 19

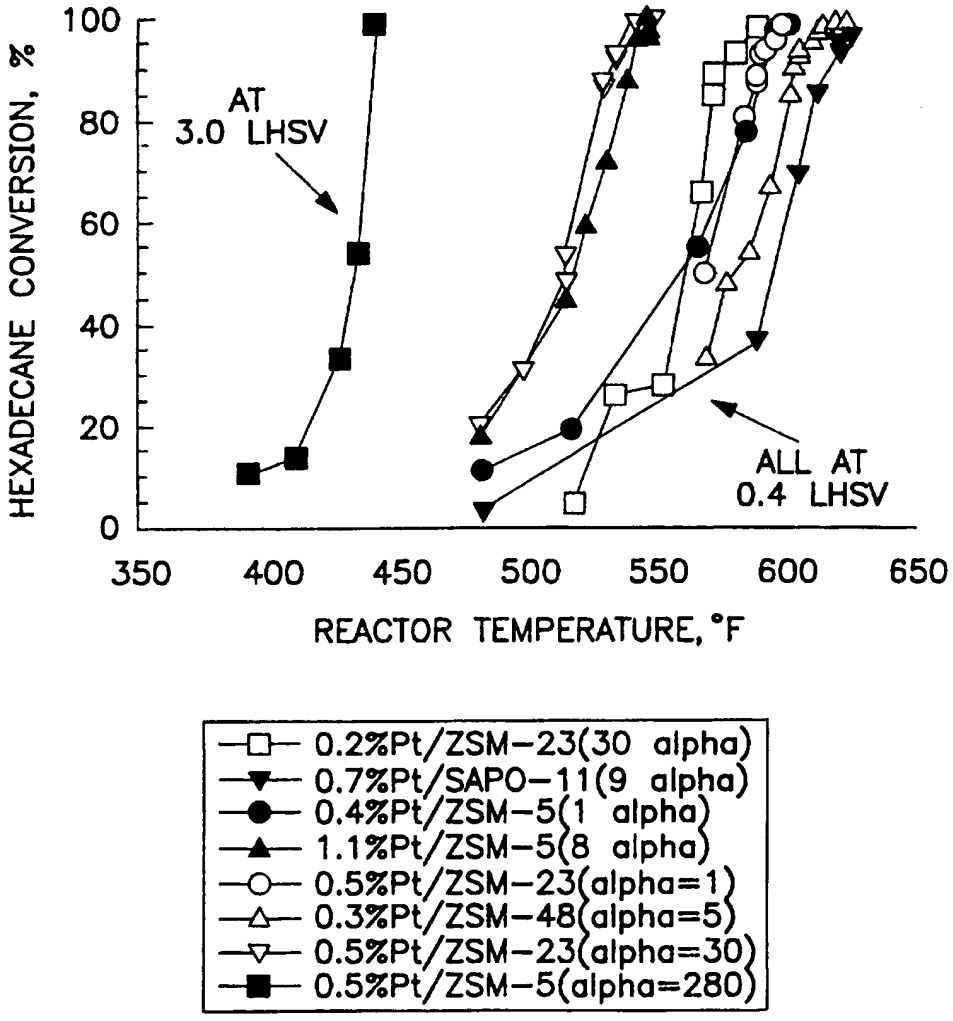


	LHSV	0.2% Pt/ ZSM-23 °C	Moly/ AL_2O_3 °C	kg/cm^2 -G H2
■	1	317	218	28.1
x	1	328	218	154.7
♦	1	334	218	28.1
F	WAXY FEED			
----	CORRELATION			

UV Absorptivity @ 226 nm can be correlated with Total Aromatics Content for a given family of hydrofinished lube stocks. It is especially useful at very low aromatics level where the repeatability of aromatics analysis becomes poor.

FIG. 20

FIG. 21


HEXADECANE CONVERSION, %
100
80
60
40
20
0
AT
3.0 LHSV
ALL AT
0.4 LHSV
350
400
450
500
550
600
650
REACTOR TEMPERATURE, °F
0.2%Pt/ZSM-23(30 alpha)
0.7%Pt/SAPO-11(9 alpha)
0.4%Pt/ZSM-5(1 alpha)
1.1%Pt/ZSM-5(8 alpha)
0.5%Pt/ZSM-23(alpha=1)
0.3%Pt/ZSM-48(alpha=5)
0.5%Pt/ZSM-23(alpha=30)
0.5%Pt/ZSM-5(alpha=280)

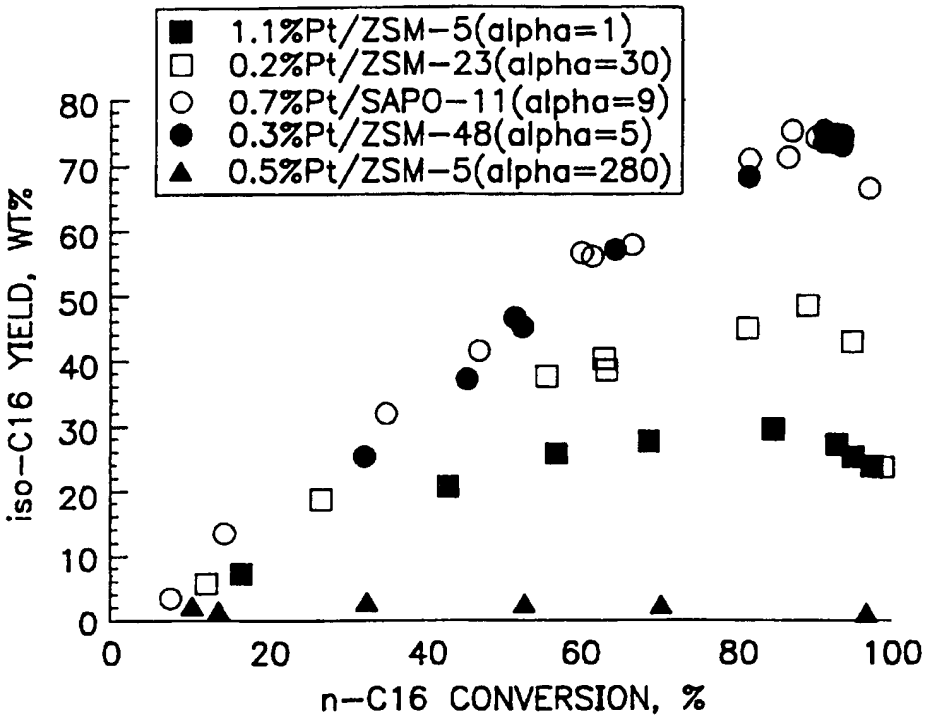

1.1%Pt/ZSM-5(alpha=1)
0.2%Pt/ZSM-23(alpha=30)
0.7%Pt/SAPO-11(alpha=9)
0.3%Pt/ZSM-48(alpha=5)
0.5%Pt/ZSM-5(alpha=280)
iso-C16 YIELD, WT%
n-C16 CONVERSION, %
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100

FIG. 22

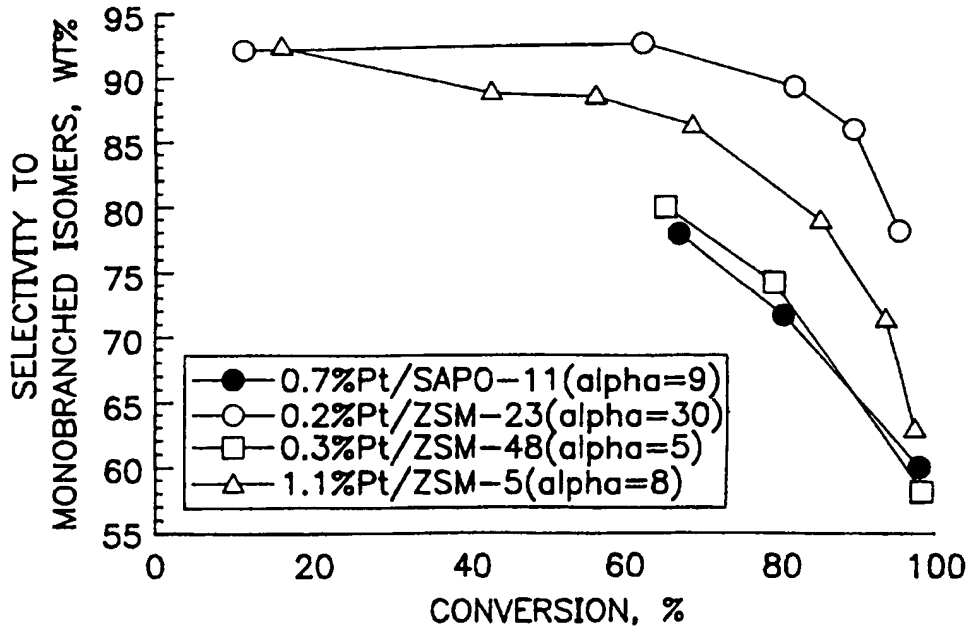

SELECTIVITY TO MONOBRANCHED ISOMERS, WT%
CONVERSION, %
0.7%Pt/SAPO-11(alpha=9)
0.2%Pt/ZSM-23(alpha=30)
0.3%Pt/ZSM-48(alpha=5)
1.1%Pt/ZSM-5(alpha=8)
55
60
65
70
75
80
85
90
95
0
20
40
60
80
100

FIG. 23

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/13945

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10G 47/00, 69/00
US CL : 208/58
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,181,598 A (GILLESPIE ET AL) 01 JANUARY 1980 (01/01/90),SEE ENTIRE DOCUTMENT , ESPECIALLY COL 1, LINES 30-57	1-33

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 24 DECEMBER 1996	Date of mailing of the international search report 17 MAR 1997
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer HELANE E. MYERS Telephone No. (703) 308-0661

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